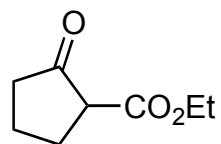
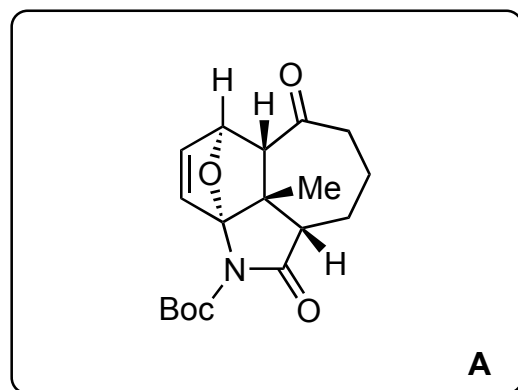


## Total Synthesis of (-)-Himalensine A

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.

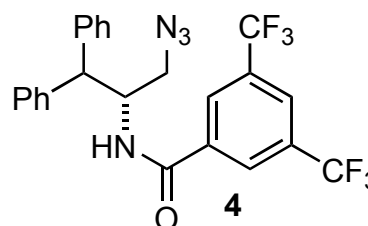
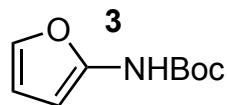


1-8



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.), PPh<sub>3</sub> (cat.) 60 °C



- 9) TFA, then, H<sub>2</sub>, Pd(OH)<sub>2</sub>, NaHCO<sub>3</sub>
- 10) NaHMDS, propargyl bromide
- 11) LiAlH<sub>4</sub> then HCl, MeOH/H<sub>2</sub>O
- 12) TIPSOTf, 2,6-lutidine
- 13) AIBN, Bu<sub>3</sub>SnH, 90 °C
- 14) CSA, 0 °C

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

*Dieckmann type reaction*

- 2) Name of the reaction?

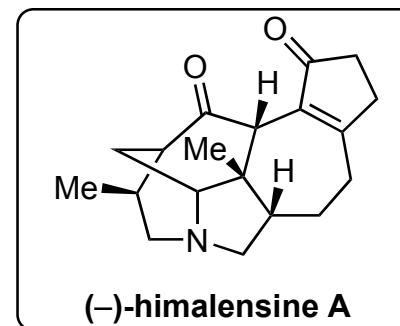
*Krapcho decarboxylation*

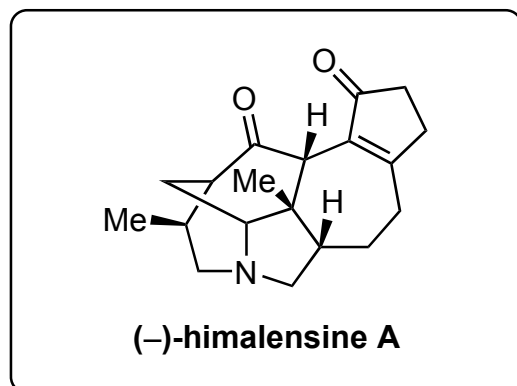
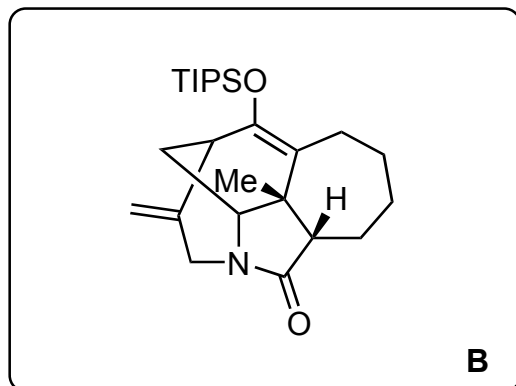
- 8) Name the reaction, provide a mechanism and describe the role of the catalyst.

*Diels-Alder / promoting prototropic shift*

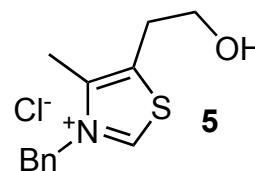
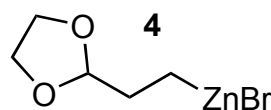
- 9) *Hint: 2 bonds are cleaved*

- 11) *Hint: only one carbonyl is affected.*  
 One of the intermediate **11'** is not fully converted during the reaction. When subjected to MsCl, Et<sub>3</sub>N, it can be converted to **12** (product of step 12). Give the structure of **11'** (byproduct of step 11).

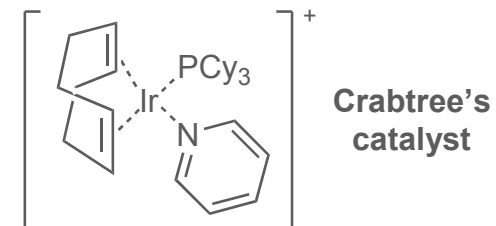




- 15) Crabtree's catalyst, H<sub>2</sub>
- 16) NBS
- 17) pyr., TsOH, oxygen, reflux
- 18) NaHMDS, -78 °C, *then*, PhNTf<sub>2</sub>
- 19) Pd<sub>2</sub>dba<sub>3</sub>, DTBPF, NMP, **4**
- 20) HCl (aq.)
- 21) **5** (cat.), Et<sub>3</sub>N, 60 °C
- 22) Vaska's catalyst (cat.), TMSD  
*then* MeOH, formic acid, 60 °C



15) Structure of the Crabtree's catalyst?



17) Name the reaction and provide a mechanism.

Kornblum DeLaMare rearrangement

19) Name of the reaction?

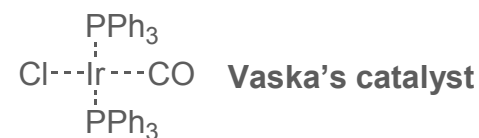
Negishi coupling

21) Name the reaction and provide a mechanism.

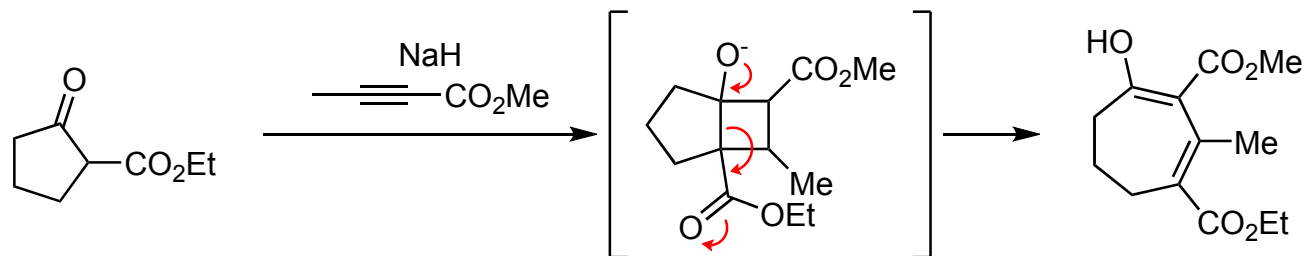
*Hint: cyclization and isomerization occurred.*

Stetter cyclization

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

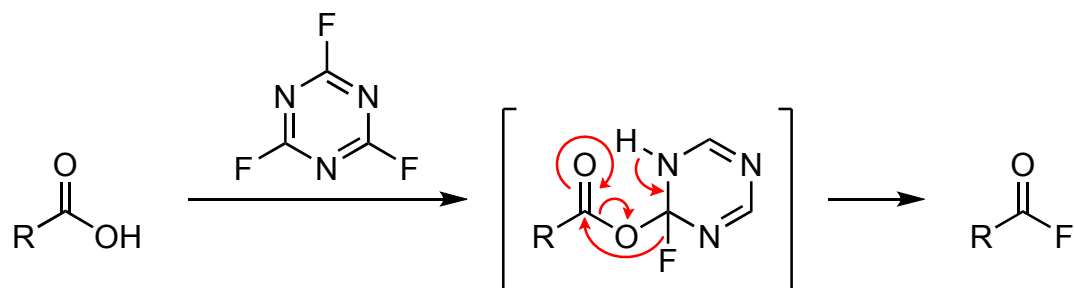


### Solution to step 1



*Org. Lett.* **2011**, *13*, 4, 664–667

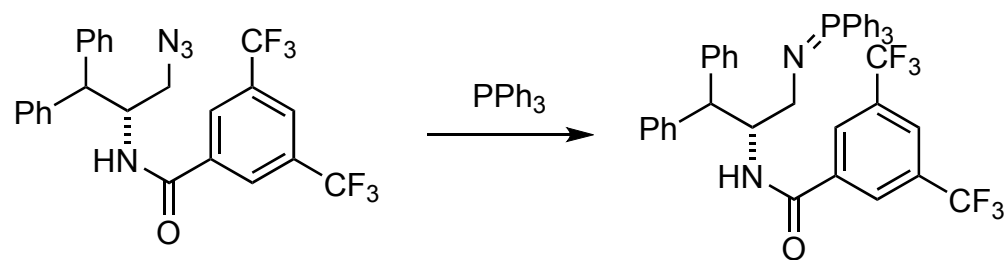
### Solution to step 5



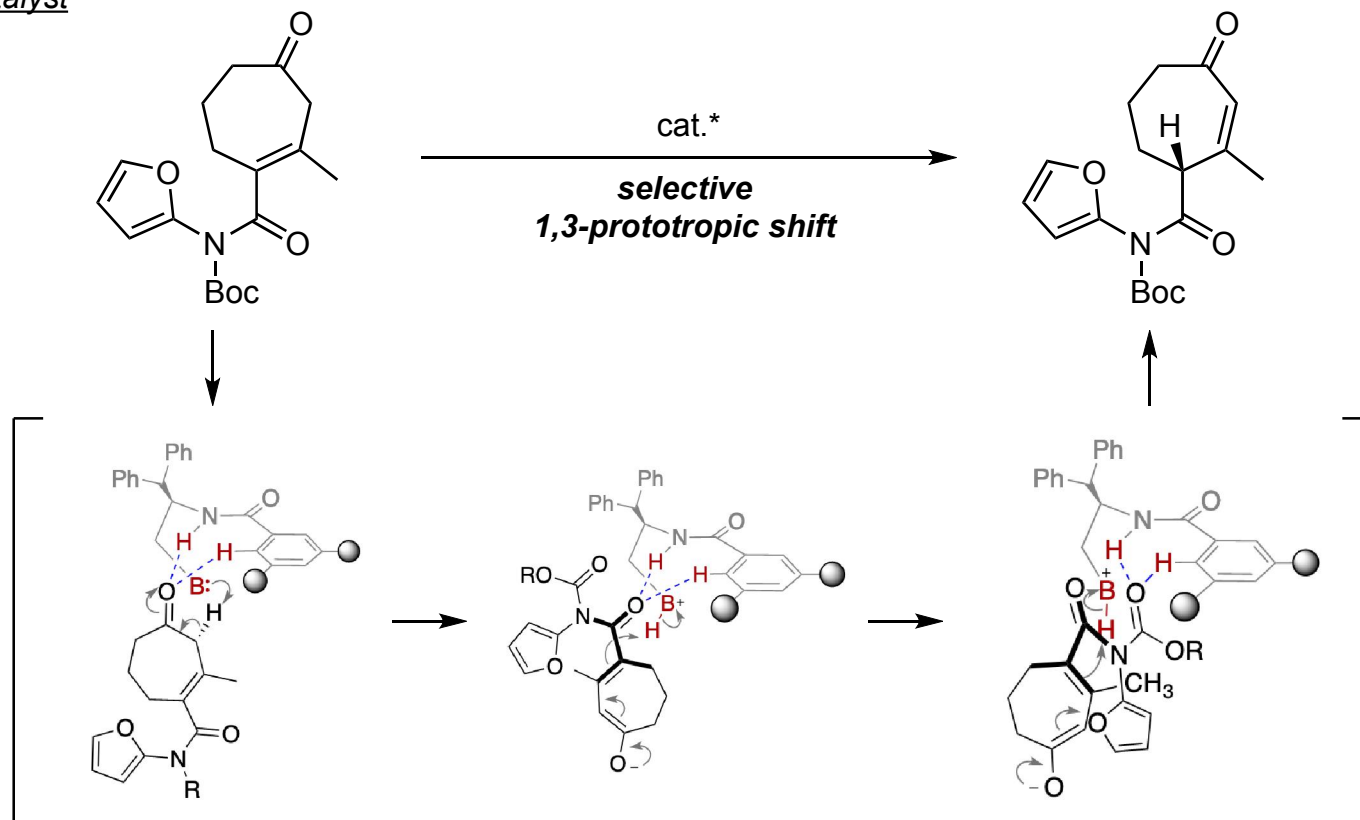
*RSC Adv.*, **2015**, *5*, 48331–48362

### Solution to step 8

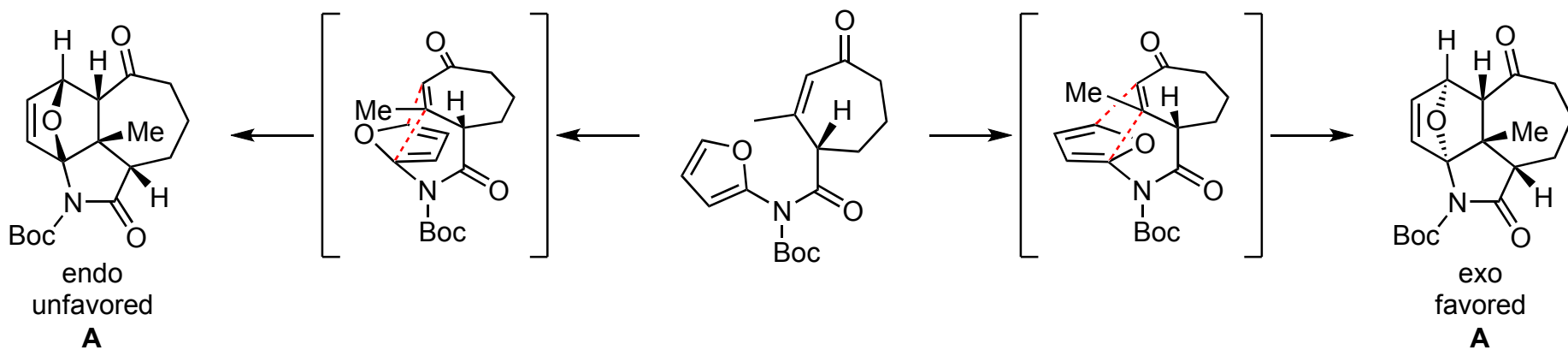
Catalyst formation in situ



Role of the catalyst

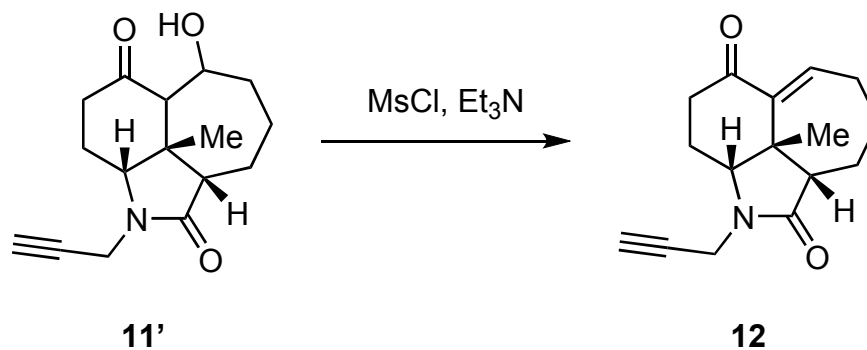


Diels-Alder reaction

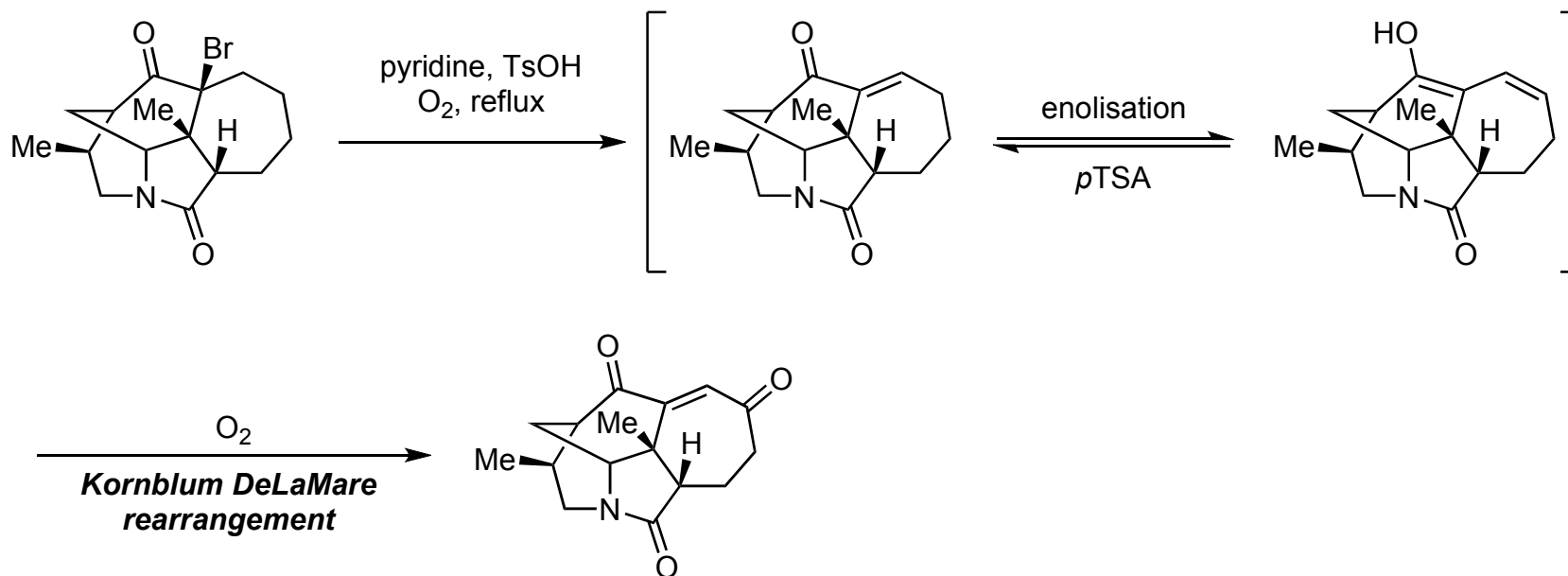


## Solution to step 11

### Intermediate 11'

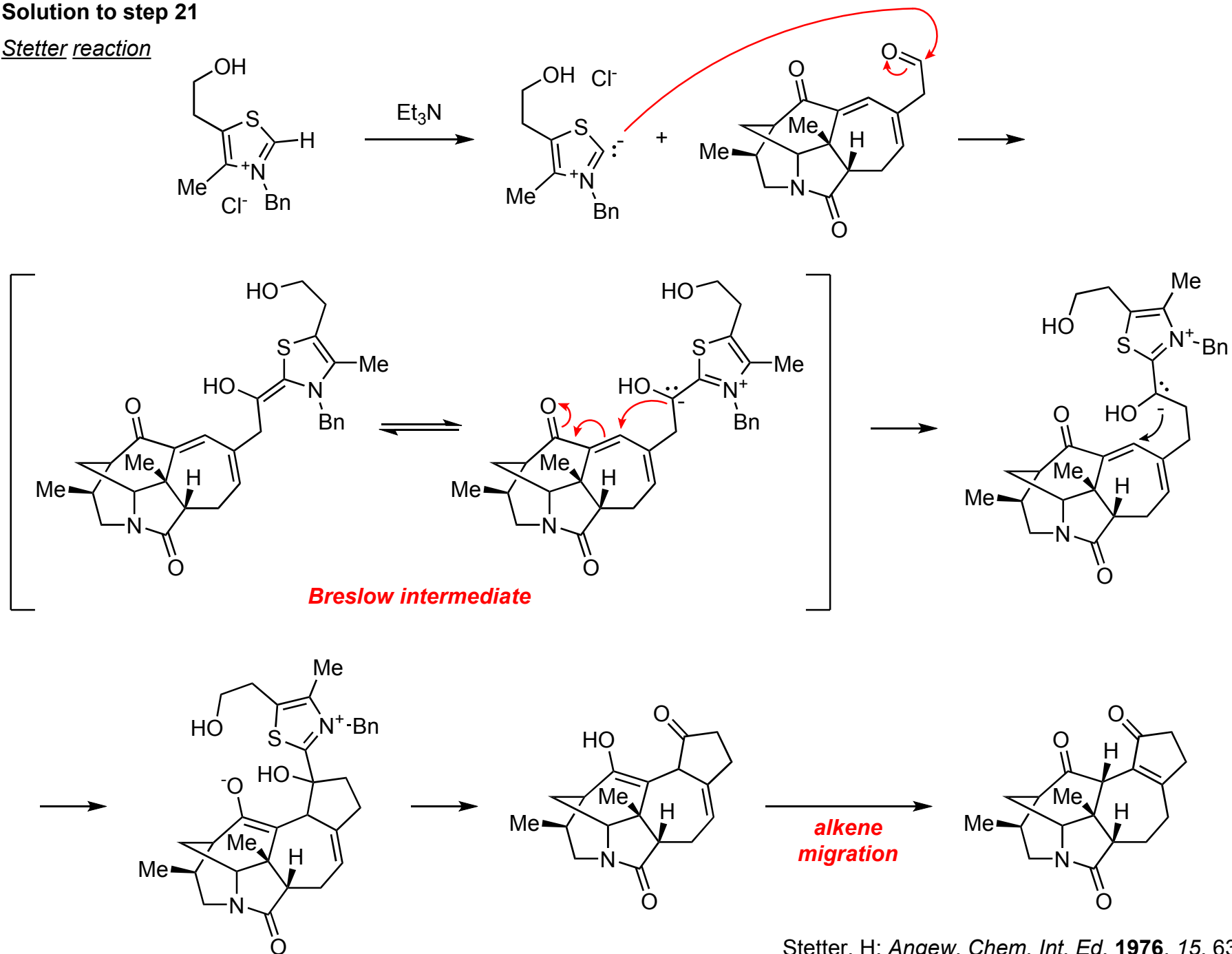


## Solution to step 17



## Solution to step 21

### Stetter reaction



Solution to step 22

