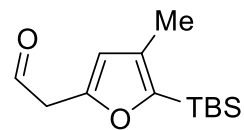
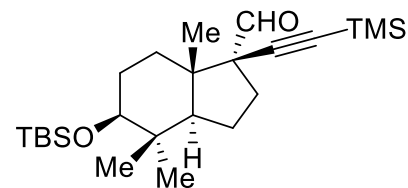


Spirochensilide A

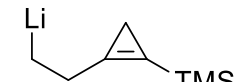
J.A.C.S, 2020, 142, 8116-8121



Fragment A



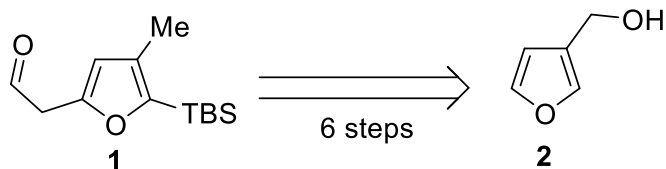
Fragment B



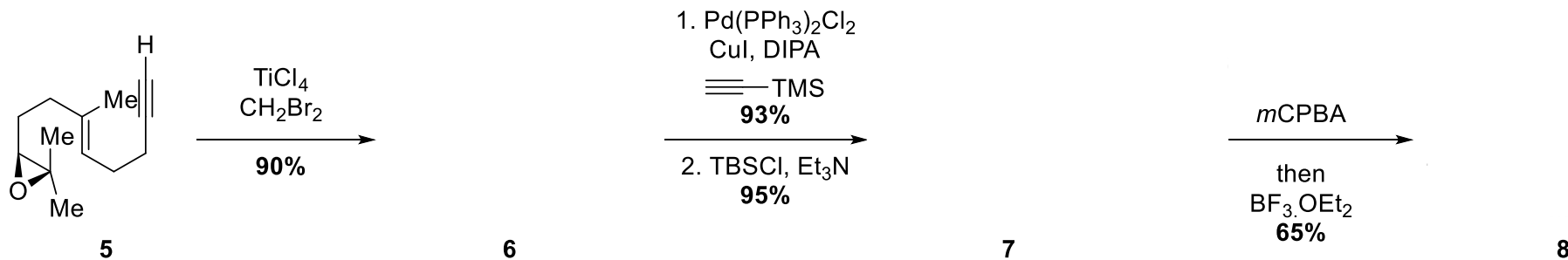
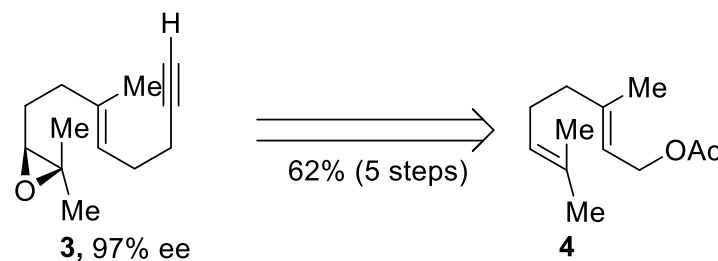
Fragment C

- Isolated by Gao from *Abies chensiensis*, endemic Chinese plant
- Antitumor, antimicrobial, antiulcerogenic, anti-inflammatory, antihypertensive, antitussive, and central nervous system activities
- Unique spirocyclic core

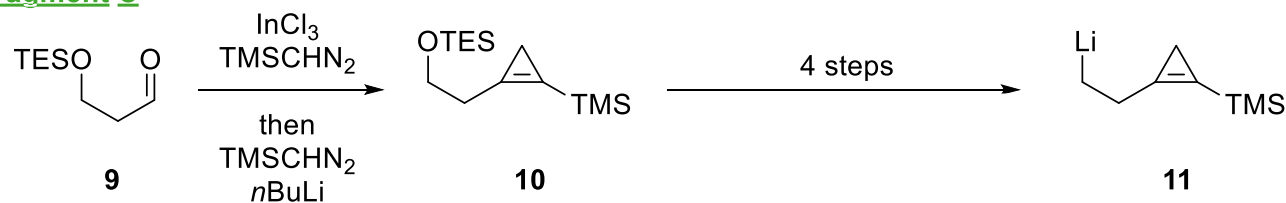
Fragment A



Fragment B

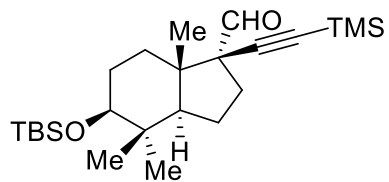


Fragment C



TMSN₂ and nBuLi then **9** added.

TES: Triethylsilyl

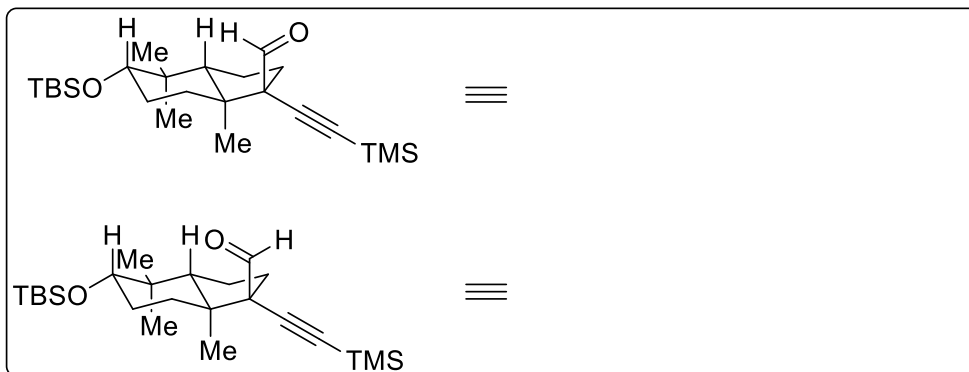


1. CeCl_3 , Fragment B (75%)

2. TESOTf, Et_3N
3. K_2CO_3 , MeOH
98% over 2 steps

12

13



$\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$

EtOH, HMPA, CO
61% yield

Name

Conditions	Yield	a : b
$\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$, EtOH, HMPA, CO	61%	1 : 1
$\text{Ni}(\text{COD})_2/\text{bipy}$, CO	84%	4 : 1
$\text{Mo}(\text{CO})_3(\text{DMF})_3$	70%	2 : 1

+

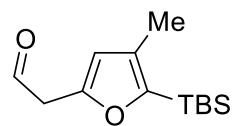
14a

14b

1. *t*BuOK, *t*BuOH (95%)

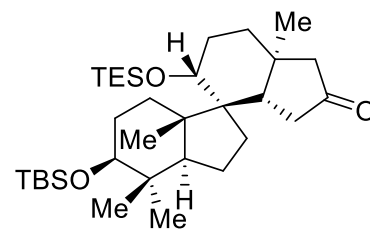
2. Pd/C, H_2 , EtOH, EtOAc

$n\text{Bu}_2\text{BOTf}$
DIPEA



17

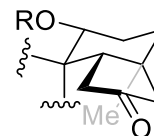
97%



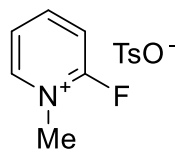
16

Li/NH₃ then DCE

80% over 2 steps



15



then neutral Al₂O₃

17

18

1. Me₂CuLi (**86%**)

2. KH, MeI (**81%**)

Methylene Blue
O₂, hν

then
ClCH₂CO₂H
(**88%**)

1. LDA, PhSeCl (**46%**)

2. *m*CPBA (**87%**)

3. DIBAL (**98%**)

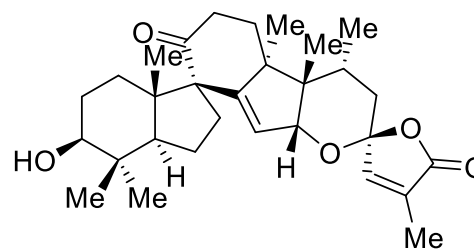
20

19

1. TBAF·3H₂O (**97%**)
2. DMP (**95%**)

3. aq. HF (**94%**)

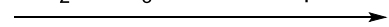
21



Spienchensilide A

If time:

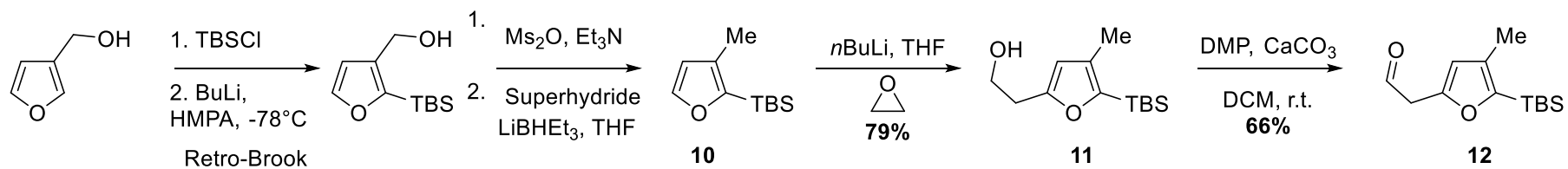
SmI_2 or Bu_3SnH : Same product



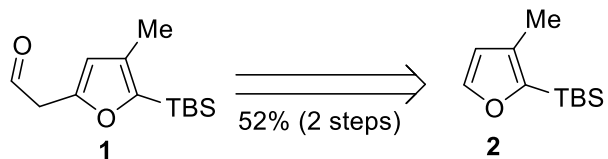
SmI_2 : 77%
 Bu_3SnH : 44%

14b

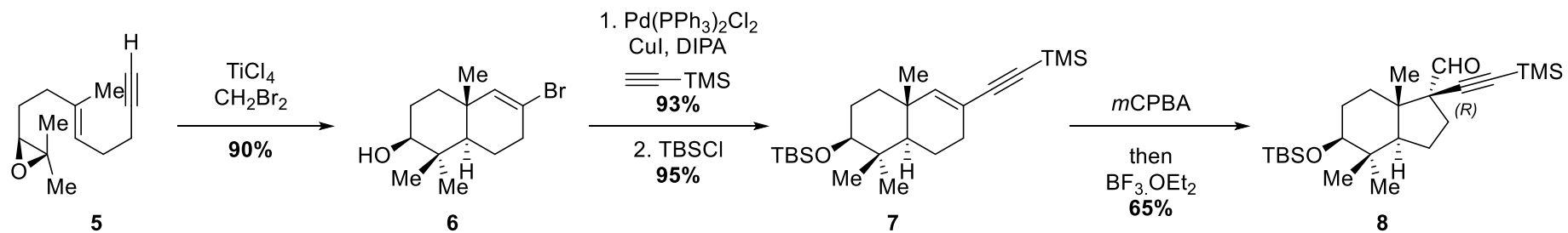
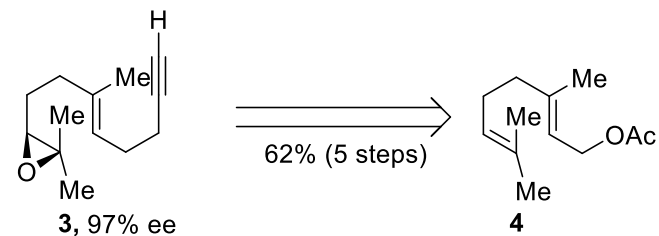
solutions



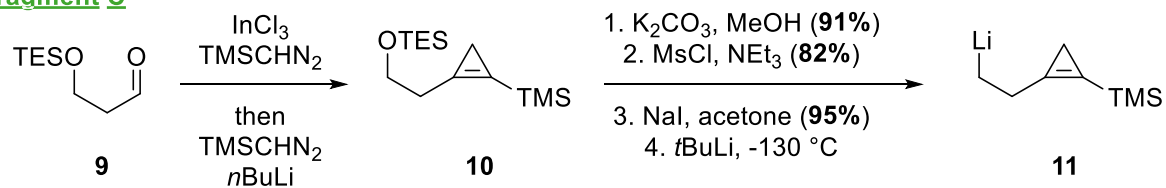
Fragment A

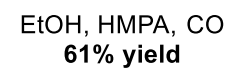
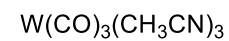
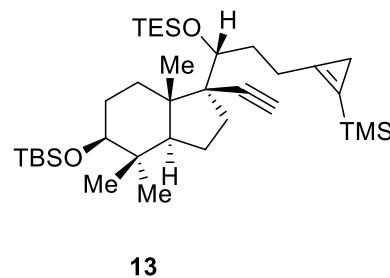
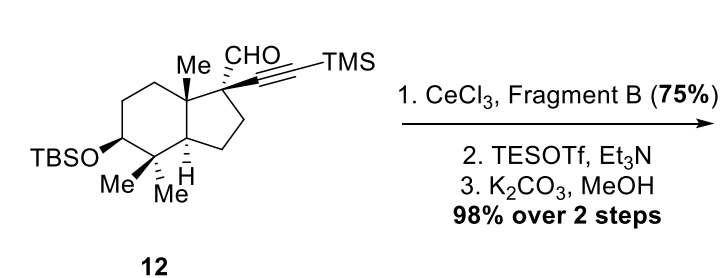


Fragment B

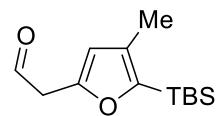
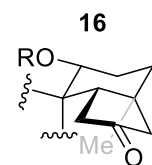
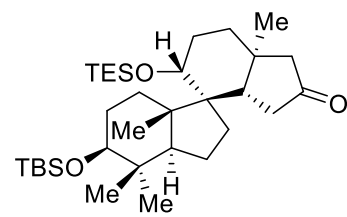
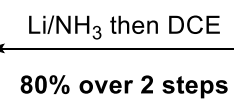
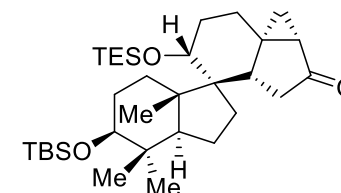
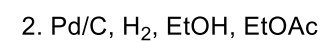
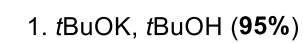
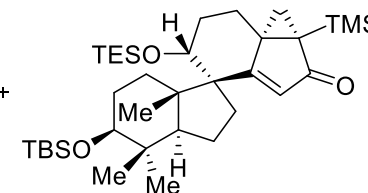
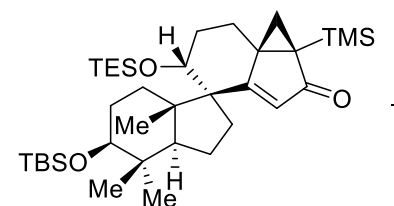
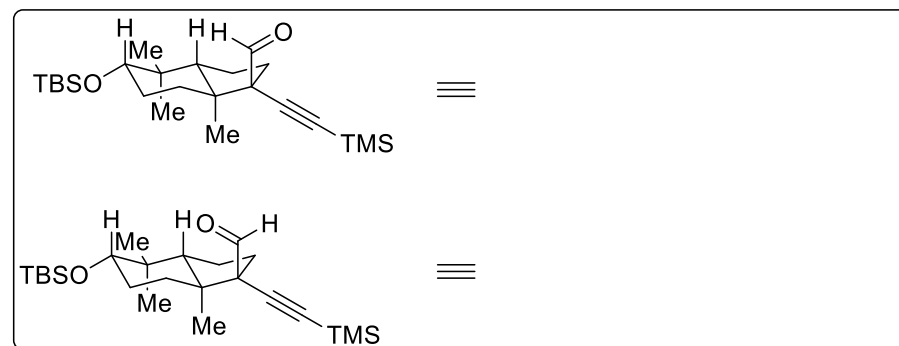


Fragment C

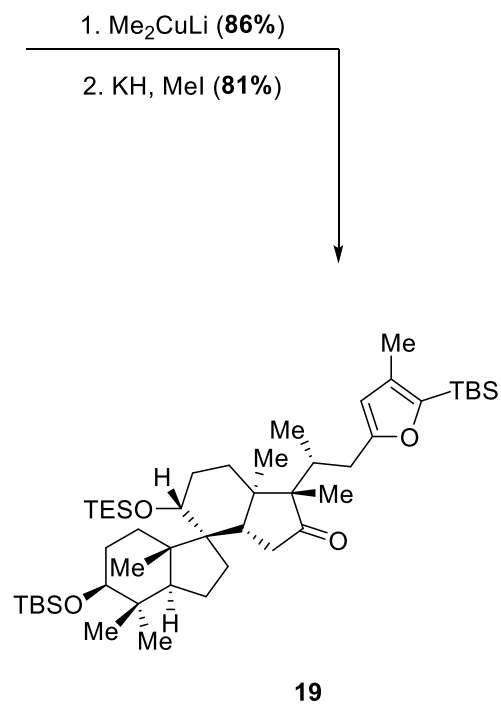
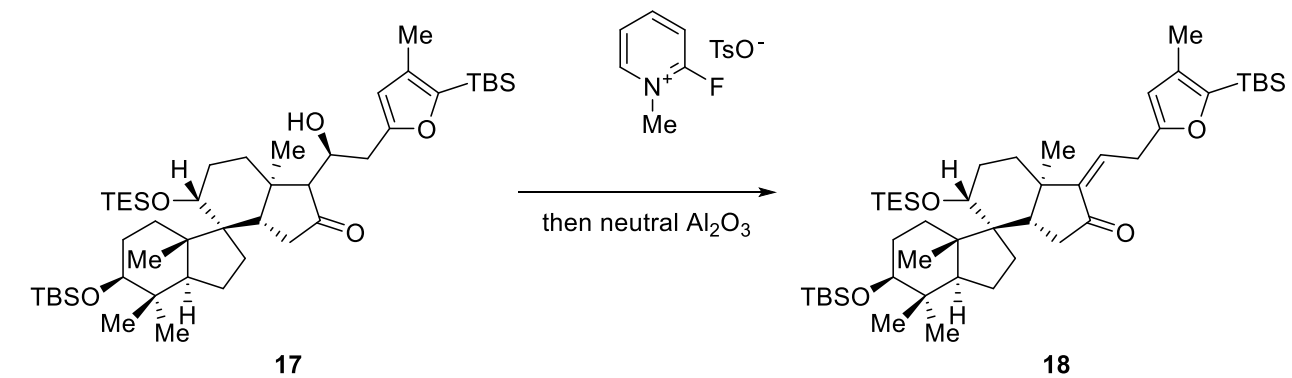




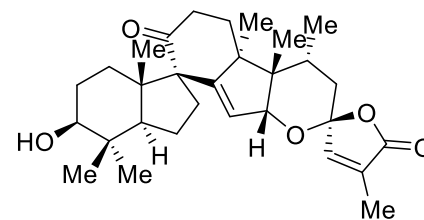
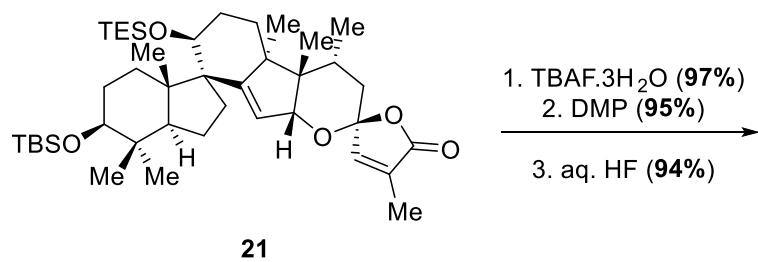
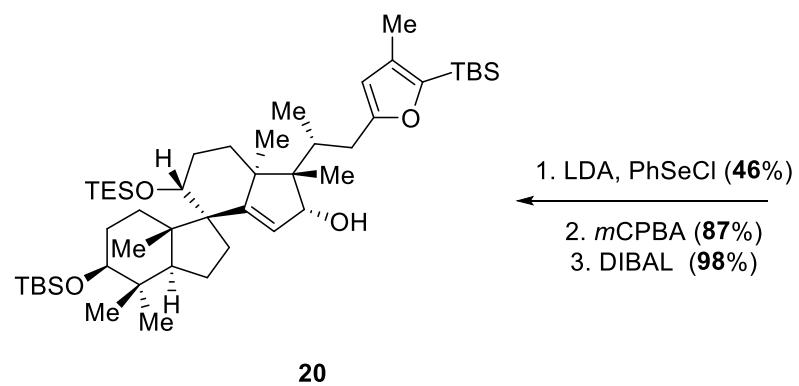
Conditions	Yield	a:b
$\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$, EtOH, HMPA, CO	61%	1:1
$\text{Ni}(\text{COD})_2/\text{bipy}$, CO	84%	4:1
$\text{Mo}(\text{CO})_3(\text{DMF})_3$	70%	2:1



97%



Methylene Blue
 O_2 , $h\nu$
 then
 $\text{ClCH}_2\text{CO}_2\text{H}$
(88%)



Spirochensilide A

If time:

