

- 1) 2 equiv. *n*-BuOTf, *i*-Pr<sub>2</sub>EtN, Et<sub>2</sub>O, -78°C,
- 2) NaOMe, MeOH
- 3) TesOTf, 2,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>, -78°C
- 4) DIBAL, CH<sub>2</sub>Cl<sub>2</sub>, -78°C

46%

**3**

- 1) (COCl)<sub>2</sub>, DMSO, Et<sub>3</sub>N, -78 °C → r.t.

- 2) Ph<sub>3</sub>PCH<sub>2</sub>(OMe)Cl, KOtBu, THF
- 3) *p*-TSA, MeOH, r.t.

82%

**4**

- 1) allyl trimethylsilane, BF<sub>3</sub>·OEt<sub>2</sub>, toluene/CH<sub>2</sub>Cl<sub>2</sub> (1:1), -78°C

71%, α:β = 4:1

- 1) TBSOTf, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, -78°C
- 2) NaI, acetone, 65°C
- 3) 2 equiv. *t*-BuLi, Et<sub>2</sub>O, 23°C

47%

**7**

- 1) **16**, CrCl<sub>2</sub>/NiCl<sub>2</sub>, DMF/THF (1:1) \*
- 2) DMP, NaHCO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>

- 3) (R)-*me*-CBS, catecholborane, CH<sub>2</sub>Cl<sub>2</sub>, 0°C

69%

\* 1:1.3

- 1) Na, NH<sub>3</sub> (l), THF, -78°C
- 2) PPh<sub>3</sub>, CCl<sub>4</sub>, DMF, 65°C
- 3) 9-BBN, THF; NaOH, H<sub>2</sub>O<sub>2</sub>
- 4) DMP, NaHCO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>

54%

**6**

**5**

- 1) (CF<sub>3</sub>O)<sub>2</sub>O, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>; Sml<sub>2</sub>
- 2) *p*-TsOH, THF/CH<sub>2</sub>Cl<sub>2</sub>/MeOH

- 3) **17**, TiCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 23°C \*
- 4) TESCl, imidazole, DMAP, CH<sub>2</sub>Cl<sub>2</sub>

28%

\* β/α = 1.3:1

**8**

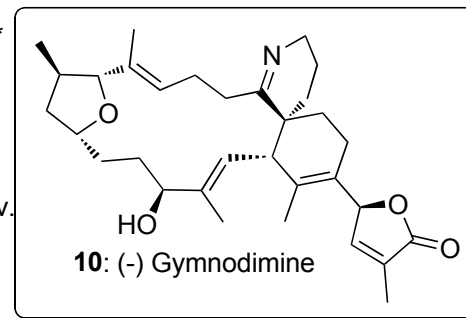
**9**

- 1) Et<sub>3</sub>N, SOCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -78°C, \*
- 2) Et<sub>3</sub>N, (Boc)<sub>2</sub>O, DMAP, CH<sub>2</sub>Cl<sub>2</sub>; hydrazine

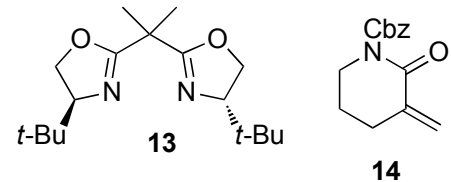
- 3) TFA, CH<sub>2</sub>Cl<sub>2</sub>, h.v.

55%

\*two isomers 3:1



**10: (-) Gymnodimine**

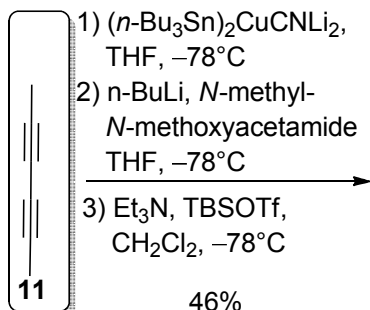


*t*-Bu

**13**

*t*-Bu

**14**



- 1) (*n*-Bu<sub>3</sub>Sn)<sub>2</sub>CuCNLi<sub>2</sub>, THF, -78°C
- 2) *n*-BuLi, *N*-methyl-*N*-methoxyacetamide, THF, -78°C
- 3) Et<sub>3</sub>N, TBSOTf, CH<sub>2</sub>Cl<sub>2</sub>, -78°C

46%

**11**

- 1) **13**, AgSbF<sub>6</sub>, CuCl<sub>2</sub>, **14**, CH<sub>2</sub>Cl<sub>2</sub> \*
- 2) *n*-BuLi, THF, -78°C
- 3) KHMDS, TsCl, THF

56%

\* *exo:endo* > 95:5

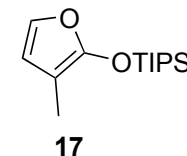
**12** 95%*ee* (major diastereo isomer)

**15**

- 1) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, *n*-BuSnH (perfusor), THF/hexane 1:6
- 2) I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -78°C, then cyclohexene

65%

**16**



**17**