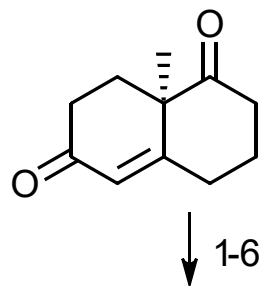


## Synthesis Challenge #69

AG Wegner  
23.11.2017



A



B

7-10



C

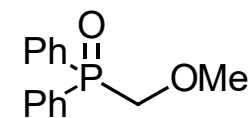
11-15



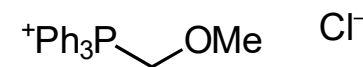
D

- 1) 1,2-ethanedithiol, 15 mol % CSA, HOAc, RT
- 2) a) NaHMDS, THF,  $-78^{\circ}$ - $0^{\circ}$ C, b)  $\text{Et}_3\text{B}$ ,  $-78^{\circ}$ C, c) MeI,  $-78^{\circ}$ -RT
- 3) a) LiHMDS, THF,  $-78^{\circ}$ - $0^{\circ}$ C b) MeOH,  $-100^{\circ}$ C-- $-90^{\circ}$ C
- 4) a) **I**, BuLi, THF,  $-78^{\circ}$ C b) then product from 3),  $-78^{\circ}$ C c) MeOH,  $-100^{\circ}$ C, 5) NaH, DMF,  $0^{\circ}$ -RT 6) TFA,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ ,  $0^{\circ}$ -RT
- 7) a) **II**, NaHMDS, THF,  $-50^{\circ}$ - $0^{\circ}$ C b) **B**,  $0^{\circ}$ -RT 8) TFA,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ ,  $0^{\circ}$ -RT 9) a) **III**, BuLi, THF,  $-7^{\circ}$ C b) Product from 9),  $-7^{\circ}$ - $0^{\circ}$ C 10)  $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ , MeCN,  $\text{CH}_2\text{Cl}_2$ ,  $0^{\circ}$ -RT
- 11) a) NaHMDS, THF,  $-78^{\circ}$ C -  $0^{\circ}$  C b)  $\text{Et}_3\text{B}$ ,  $-70^{\circ}$ C c) MeI,  $-70^{\circ}$ C-RT
- 12) a) LiHMDS, THF,  $-78^{\circ}$ C- $0^{\circ}$ C b) MeOH,  $-100^{\circ}$ C-- $-90^{\circ}$ C
- 13) Li,  $\text{NH}_3$ , *t*BuOH,  $\text{Et}_2\text{O}$ ,  $-78^{\circ}$ C
- 14) TMSI, HMDS, MeCN, RT
- 15) a) MeLi, THF,  $0^{\circ}$ C b) **IV**,  $-78^{\circ}$ C

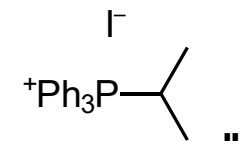
Please provide a synthesis for A.



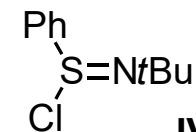
**I**



**II**



**III**



**IV**

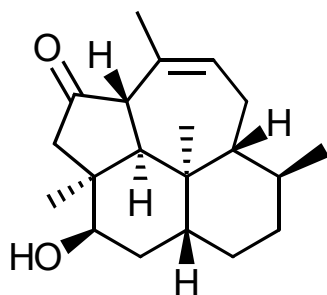
↓ 16-19



↓ 20-25



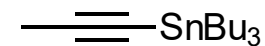
↓ 26-31



- 16) a) **V**, BuLi, THF, -78°C
- b) Me<sub>3</sub>Al, -78°C,
- c) then **D**, TBSOTf, -100°C--80°C
- 17) a) 38% aq. HF, MeCN, CH<sub>2</sub>Cl<sub>2</sub>
- b) 2 N HCl, RT
- 18) a) MeLi, THF, 0°C
- b) allyl iodide, HMPA, -30°C-0°C
- 19) toluene, 120°C (sealed tube)

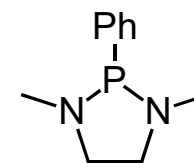
- 20) L-selectride, THF, -78°C-RT
- 21) 3 mol % Grubbs II, CH<sub>2</sub>Cl<sub>2</sub>, reflux
- 22) TBSOTf, 2,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>,
- 23) OsO<sub>4</sub>, 3,5-lutidine, THF, toluene
- 24) 1,1,1-trifluoroacetone, oxone, NaHCO<sub>3</sub>, (Na)<sub>2</sub>EDTA, DMM, MeCN, H<sub>2</sub>O, 0°C,
- 25) 1,1'-thiocarbonyldiimidazole, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, RT

- 26) a) **VI**, THF, 57°C
- 27) silica gel, pentane/Et<sub>2</sub>O (20:1-9:1)
- 28) 38% aq. HF, MeCN, CH<sub>2</sub>Cl<sub>2</sub>, RT
- 29) PhSH, LiOH·H<sub>2</sub>O, THF, 60°C
- 30) 30 % aq. H<sub>2</sub>O<sub>2</sub>, HFIP, RT
- 31) P(OMe)<sub>3</sub>, toluene, 100 °C,



**V**

DMM=dimethoxymethane



**VI**