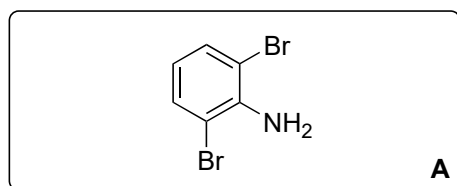


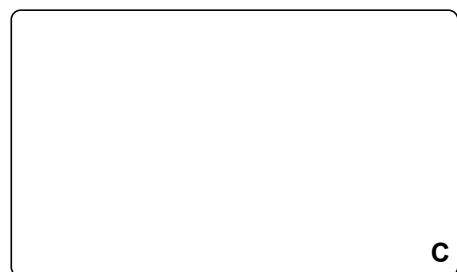
# An Enantioselective Total Synthesis of (+)-Citrinadin B

Kong, K; Enquist, J.; McCallum, M; Smith, G.; Matsumaru, T.; Wood, J. L.

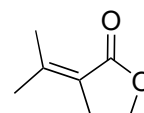
*J. Am. Chem. Soc.* **2013**, 135, 10890-10893.



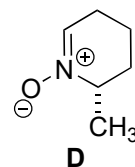
1–9



10–12

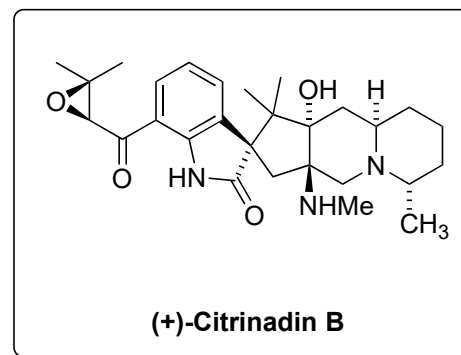


- 1)  $\text{AlMe}_3$ , toluene, **B**
- 2) TBSCl, imidazole
- 3)  $\text{Pd}(\text{OAc})_2$ ,  $\text{PPh}_3$ ,  $\text{Et}_3\text{N}$ , 1%  $\text{H}_2\text{O}$ , toluene, reflux
- 4)  $\text{NaH}$ ,  $\text{BnBr}$ , DMF
- 5) TBAF
- 6) DMSO,  $(\text{ClCO})_2$ ,  $\text{Et}_3\text{N}$
- 7)  $\text{HC}\equiv\text{CMgBr}$
- 8) TBSCl, imidazole
- 9)  $\text{Pd}_2(\text{dba})_3$ ,  $\text{Et}_3\text{SiH}$ , AcOH, toluene, rt



- 10) TBAF
- 11) DMSO,  $(\text{ClCO})_2$ ,  $\text{Et}_3\text{N}$
- 12) 3 eq. **D**, L-proline,  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ , rt, 9 days

Please provide a mechanism for step 9.

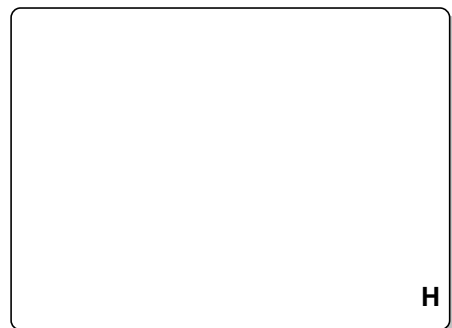




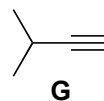
13–17



18–20

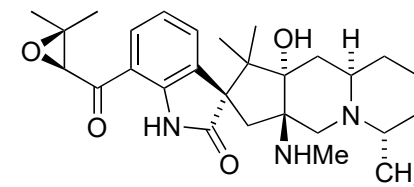


- 13)  $\text{Me}_3\text{SOI}$ , NaH, THF/DMSO
- 14) TMSCl, NaI, THF/ $\text{CH}_3\text{CN}$
- 15) Zn, AcOH/THF
- 16) MsCl,  $\text{Et}_3\text{N}$
- 17)  $\text{K}_2\text{CO}_3$ , MeOH



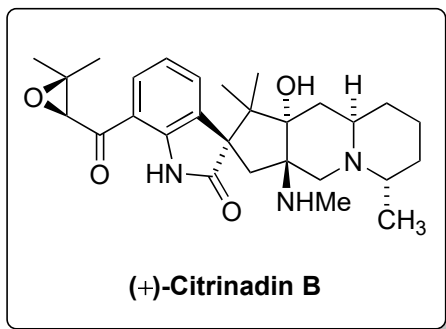
- 18) **G**,  $\text{PdCl}_2(\text{PPh}_3)_2$ , CuI, *i*-Pr<sub>2</sub>NH, DMF, 80 °C
- 19) *t*-BuLi, O<sub>2</sub>
- 20)  $\text{MgCl}_2$ , NaN<sub>3</sub>,  $\text{CH}_3\text{CN}$ , 60 °C

Please provide a mechanism for step 19.

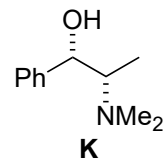
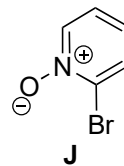


(+)-Citrinadin B

21–26



- 21) 1.5 eq. **J**, (Ph<sub>3</sub>P)AuNTf<sub>2</sub>, THF
- 22) **K**, Et<sub>2</sub>Zn, O<sub>2</sub>, toluene
- 23) (Boc)<sub>2</sub>O, Et<sub>3</sub>N, DMAP
- 24) H<sub>2</sub>, Pd/C
- 25) Me<sub>3</sub>OBf<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>
- 26) Mg(ClO<sub>4</sub>)<sub>2</sub>, CH<sub>3</sub>CN, 60 °C



Please provide a mechanism for step 21.