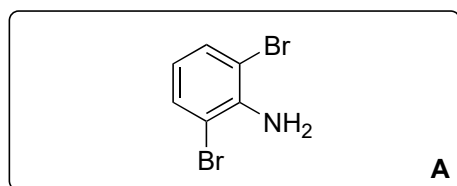


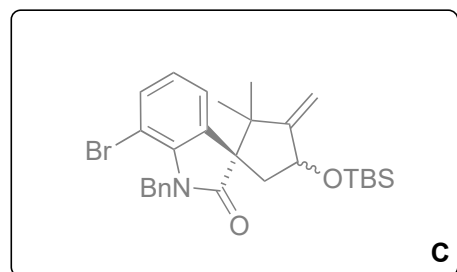
# An Enantioselective Total Synthesis of (+)-Citrinadin B

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

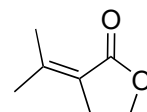
*J. Am. Chem. Soc.* **2013**, *135*, 10890–10893.



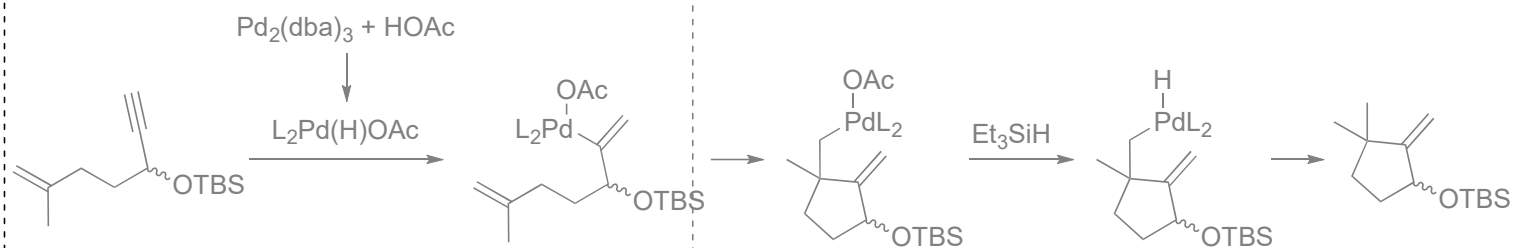
1–9



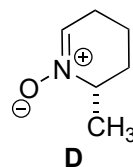
10–12



- 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

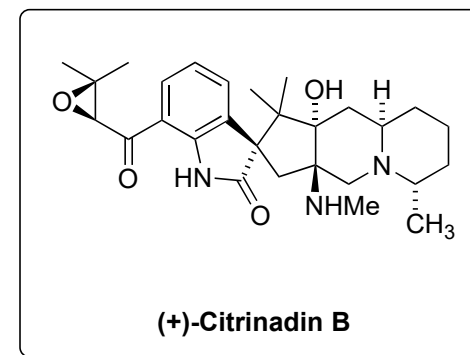


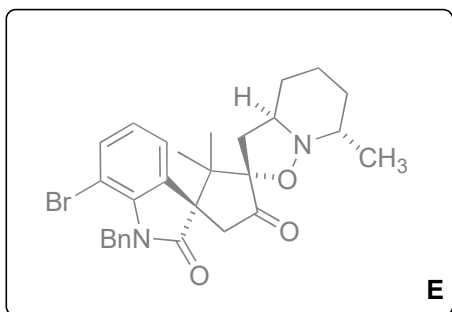
Trost *JACS* **1987**, *109*, 3163–3165.



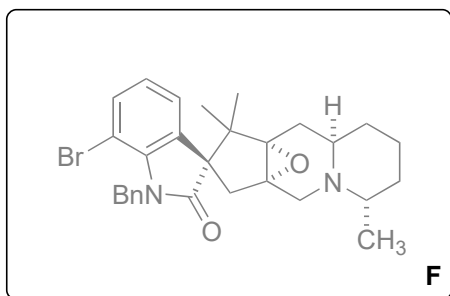
- 10) TBAF
- 11) DMSO,  $(\text{ClCO})_2$ ,  $\text{Et}_3\text{N}$
- 12) 3 eq. **D**, L-proline,  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ , rt, 9 days

Please provide a mechanism for step 9.

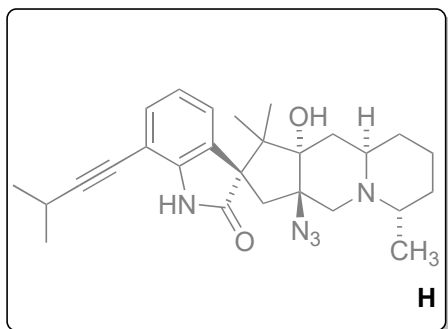




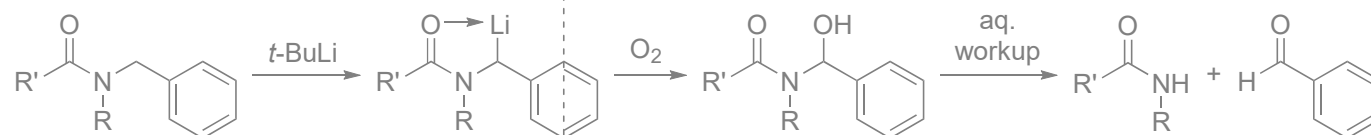
13–17



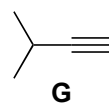
18–20



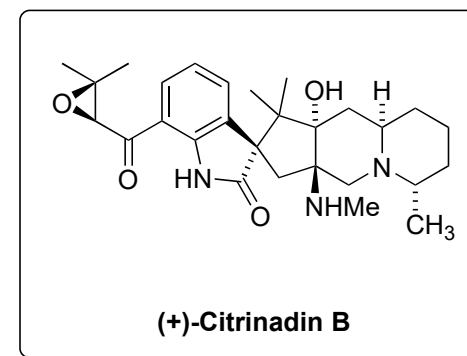
- 13)  $\text{Me}_3\text{SOI}$ , NaH, THF/DMSO
- 14) TMSCl, NaI, THF/ $\text{CH}_3\text{CN}$
- 15) Zn, AcOH/THF
- 16) MsCl,  $\text{Et}_3\text{N}$
- 17)  $\text{K}_2\text{CO}_3$ , MeOH



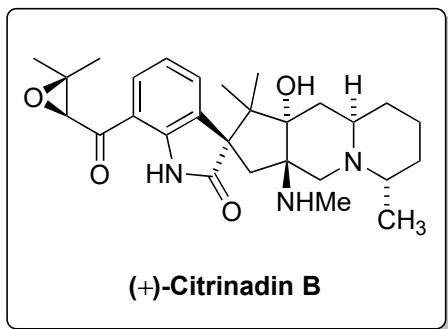
- 18) **G**,  $\text{PdCl}_2(\text{PPh}_3)_2$ , CuI, *i*-Pr<sub>2</sub>NH, DMF, 80 °C
- 19) *t*-BuLi, O<sub>2</sub>
- 20)  $\text{MgCl}_2$ , NaN<sub>3</sub>,  $\text{CH}_3\text{CN}$ , 60 °C



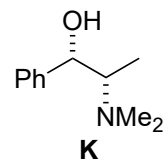
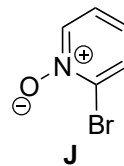
Please provide a mechanism for step 19.



21–26



- 21) 1.5 eq. **J**,  $(\text{Ph}_3\text{P})\text{AuNTf}_2$ , THF
- 22) **K**,  $\text{Et}_2\text{Zn}$ ,  $\text{O}_2$ , toluene
- 23)  $(\text{Boc})_2\text{O}$ ,  $\text{Et}_3\text{N}$ , DMAP
- 24)  $\text{H}_2$ , Pd/C
- 25)  $\text{Me}_3\text{OBF}_4$ ,  $\text{Na}_2\text{CO}_3$
- 26)  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{CH}_3\text{CN}$ ,  $60\text{ }^\circ\text{C}$



Please provide a mechanism for step 21.

