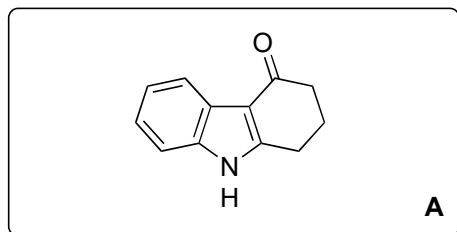


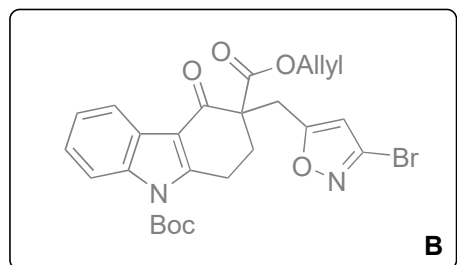
Asymmetric Total Syntheses of Kopsia Indole Alkaloids

L. Leng, X. Zhou, Q. Liao, F. Wang, H. Song, D. Zhang, X. Liu, Y. Qin

Angew. Chem. Int. Ed. **2017**, *56*, 3703–3707.

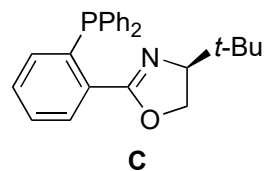


1–3



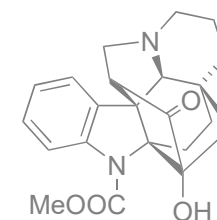
4–7

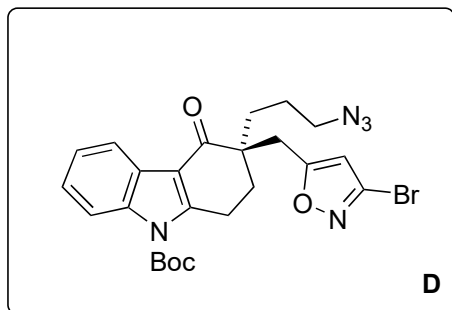
- 1) (Boc)₂O, DMAP, CH₂Cl₂
- 2) LiHMDS, THF *then* allyl chloroformate, –78 °C
- 3) 3-bromo-5-(bromomethyl) isoxazole, K₂CO₃, acetone, 56 °C



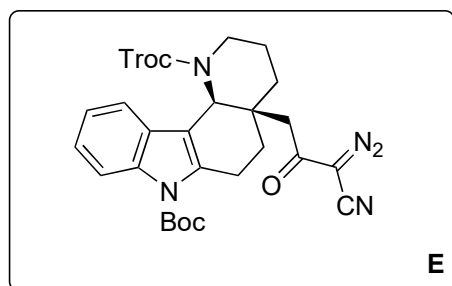
- 4) [Pd₂(dba)₃], **C**, PhMe
- 5) benzo[d][1,3,2]dioxaborole, [RhCl(PPh₃)₃], THF *then* NaBO₃·H₂O, THF/H₂O
- 6) MsCl, Et₃N, CH₂Cl₂
- 7) NaN₃, DMF, 60 °C

Please Name the reaction in step 4.
Tsuji–Trost decarboxylative allylation
How would you synthesize ligand **C** and what is the trivial name?
t-BuPhOX, *Org. Synth.* **2009**, *86*, 181





8-12

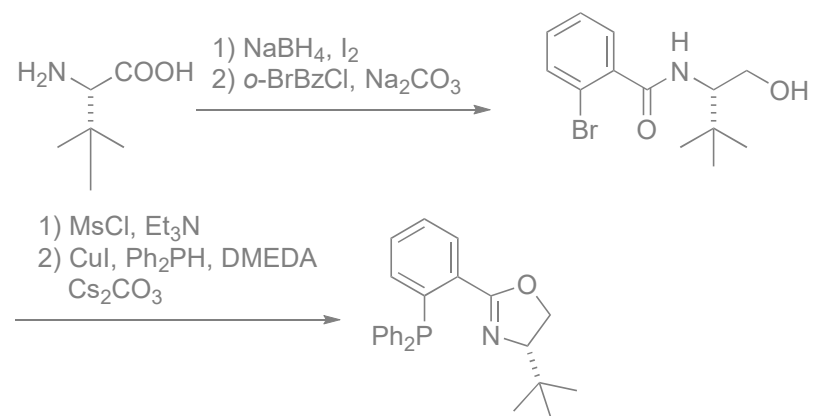


13-15

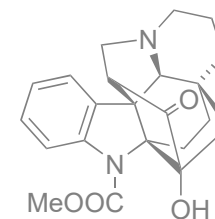
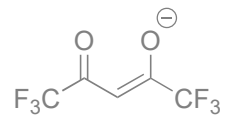
- 8) PPh₃, THF/H₂O, reflux
- 9) NaBH₄, EtOH/THF
- 10) TrocCl, Na₂CO₃, CH₂Cl₂/H₂O
- 11) FeCl₂, CH₃CN, reflux
- 12) 1H-imidazole-1-sulfonyl azide, pyridine

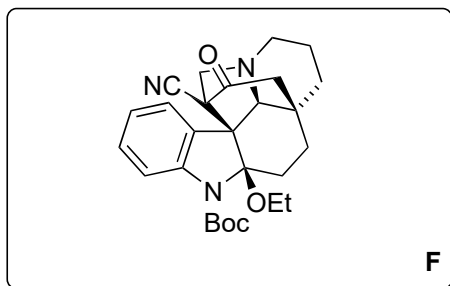
- 13) [Cu(hfacac)₂], chlorobenzene, 120 °C
- 14) Zn, EtOH/THF/AcOH
- 15) CH₂O (30% aq.), EtOH, reflux

synthesis of *t*-BuPhOX

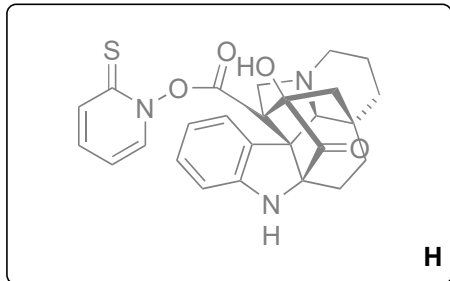


Structure of hfacac?



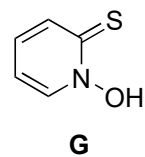


16-20

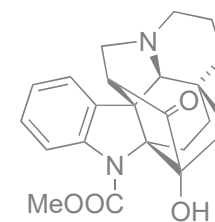


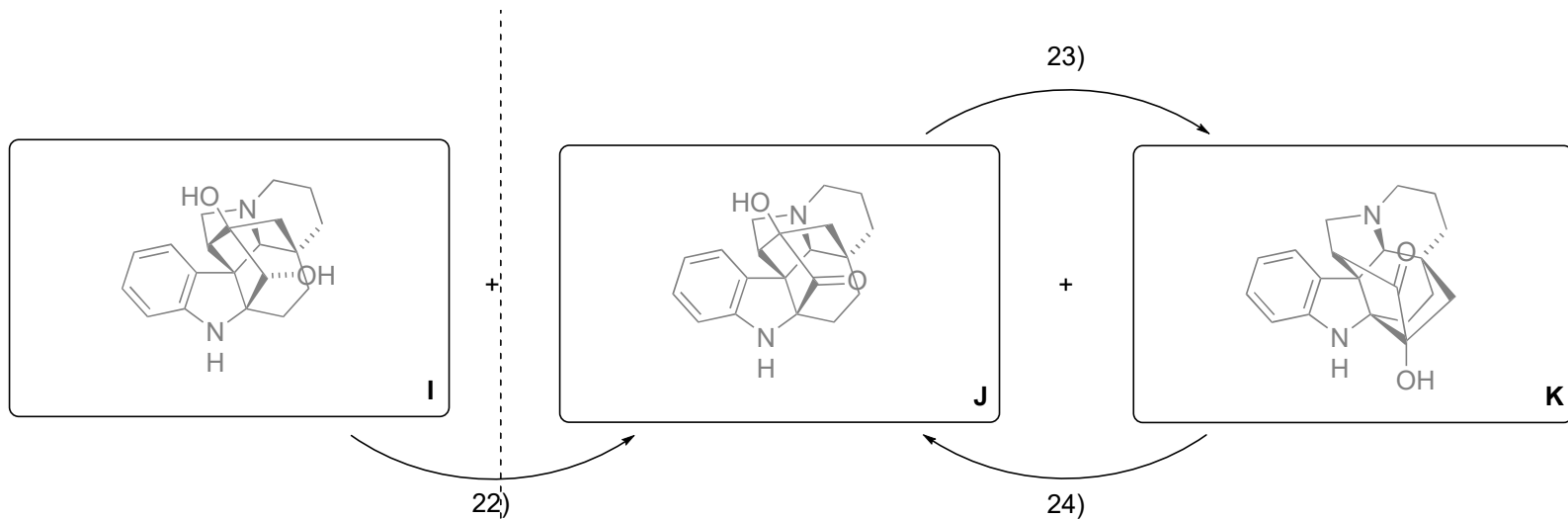
21

- 16) $\text{CF}_3\text{CO}_2\text{H}$, CH_2Cl_2 , 0 °C to 23 °C
 17) TMSCN , AlCl_3 , CH_2Cl_2
 18) SmI_2 , THF
 19) HCl (conc.), 100 °C
 20) **G**, EDCI, DMAP, CH_2Cl_2



- 21) AIBN, *n*- Bu_3SnH , benzene, reflux

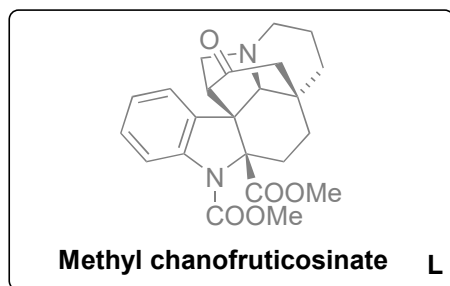




22) DMP, CH₂Cl₂
 23) NaOH aq./1,4-dioxane
 24) NaOH aq./1,4-dioxane

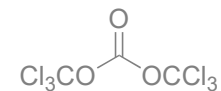
J

25–27



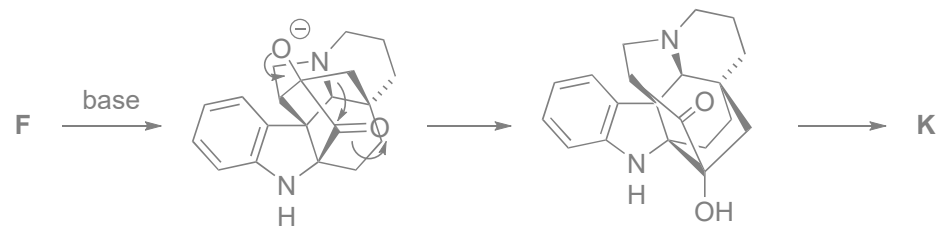
25) triphosgene, pyridine CH₂Cl₂, 0 °C then MeOH reflux
 26) MeOH/pyridine/H₂O, 70 °C
 27) Pb(OAc)₄, MeOH,

What is the structure of triphosgene?



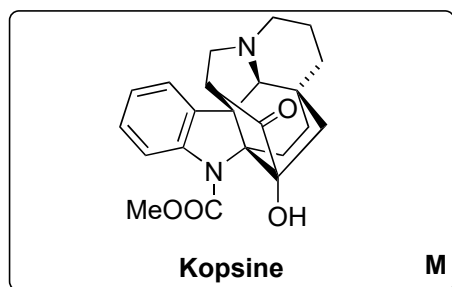
If **J** is heated in benzene for 1 h, a 1:1 mixture of **J** and **K** was obtained.
 Please classify the reaction and give a mechanism.

acyloin rearrangement



K

28



28) BTC, pyridine CH_2Cl_2 , 0°C then MeOH reflux

Please give a sequence for the following transformation.

