Total Syntheses of (–)-Deoxoapodine, (–)-Kapsifoline D and (–)-Beninine

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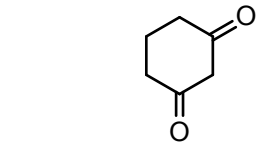


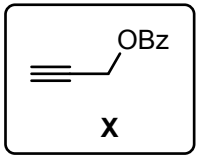
1-4

A

5-9

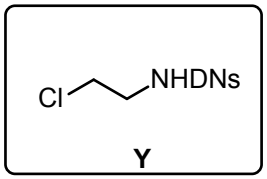
B

1) Tf_2O (1.5 equiv), 2,6-lutidine
2) **X**, $PdCl_2(PPh_3)_2$, CuI
3) CBS-Cat, Catecholborane
4) *o*-Nitrophenol, $(EtO)_3CCH_3$



X

5) K_2CO_3, EtOH
6) Lindlar-Cat, H_2
7) **Y**, PPh_3, DIAD
8) CrO_3, TBHP
9) PhONa

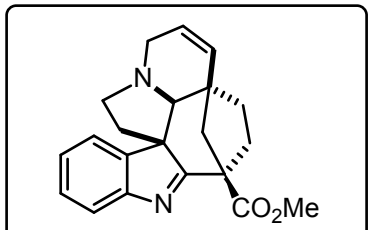


Y

Name of step 4 and characterization?

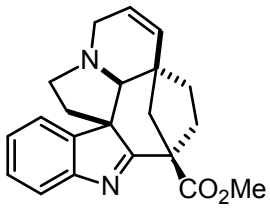
Name and structure of protecting group of **Y**?

Mechanism for step 9?



(–)-Kapsifoline D

10-17



(–)-Kapsifoline D

10) $PhNHNH_2$, TFA
11) TFA, Et_3SiH
12) $LiAlH_4$
13) TBSCl, imH
14) $(COCl)_2$, DMSO, Et_3N
15) *n*-BuLi, Mander's reagent
16) TBAF
17) TsCl, Et_3N, *t*-BuOK

Name, mechanism and characterization of key-step of 10
hint: two products isolated

Structure of Mander's reagent?