Diastereoselective Total Synthesis of (±)-Basiliolide B

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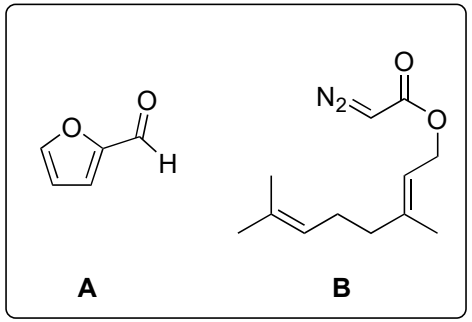
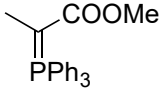


1–6

1) DBU, IBX, DMSO
2) $Cu(TBS)_2$, toluene, 80 °C
3) $NaBH_4$
4) KOH, EtOH, *then* allylBr
5) PPh_3, I_2, imidazole
6) *n*-BuLi, THF, -80 °C, 15 min

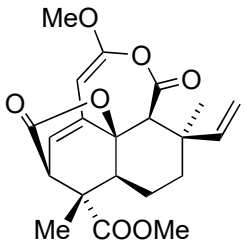
C

7–9

7) *m*-CPBA
8) $NaIO_4$
9) 

Please come up with a synthesis of diazoacetate **B**.

In step 6 only one diastereomer is formed. Can you explain that selectivity?



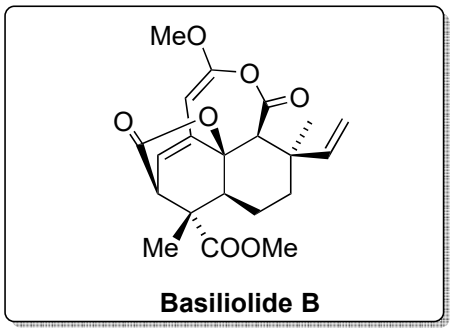
Basiliolide B

D

10–15

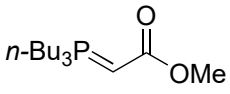
F

16+17



Basiliolide B

10) $VO(acac)_2$, TBHP
11) Ag_2O, MeI
12) **E**, toluene, 100 °C
13) CrO_3, H_2SO_4
14) DABCO, toluene, 70 °C
15) 120 °C, toluene, sealed tube



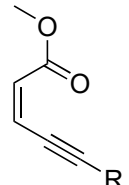
E

16) $Pd(PPh_3)_4$, PPh_3, pyrrolidine
17) Tf_2O, Et_3N

Please provide a mechanism for the name reaction of step 10.

Please provide two possible transition states which explain the diastereoselectivity of step 15.

The Dudley and the Stoltz group used a different approach to furnish the alpha-pyrone, starting from **G**. Please name the reaction and come up with a mechanism. Which other methods for the synthesis of alpha-pyrones do you know?



G