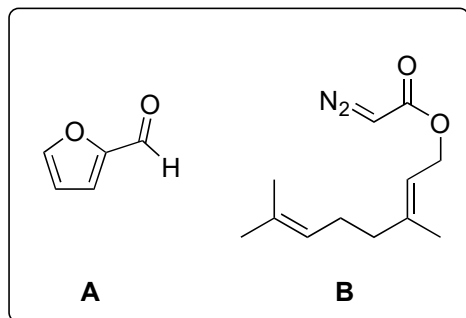


Diastereoselective Total Synthesis of (±)-Basiliolide B

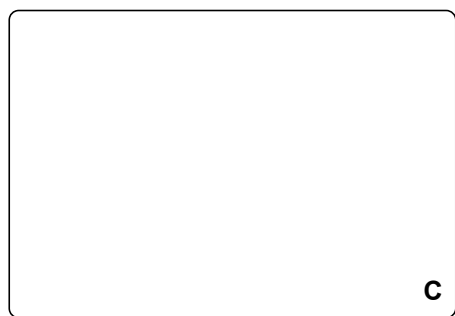
X. Liang, L. Zhou, L. Min, W. Ye, W. Bao, W. Ma, Q. Yang, F. Qiao, X. Zhang, and C.-S. Lee

Angew. Chem. Int. Ed. **2014**, *53*, 11294–11297.

J. Org. Chem. **2017**, *82*, 3463–3481.



1–6



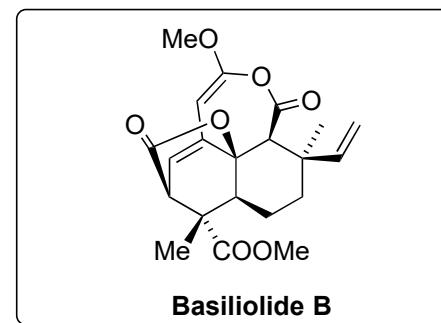
7–9

- 1) DBU, IBX, DMSO
- 2) Cu(TBS)₂, toluene, 80 °C
- 3) NaBH₄
- 4) KOH, EtOH, *then* allylBr
- 5) PPh₃, I₂, imidazole
- 6) *n*-BuLi, THF, -80 °C, 15 min

- 7) *m*-CPBA
- 8) NaIO₄
- 9)

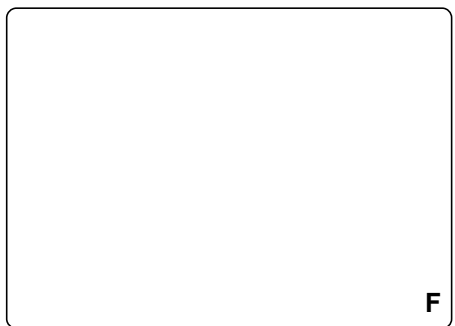
Please come up with a synthesis of diazoacetate **B**.

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

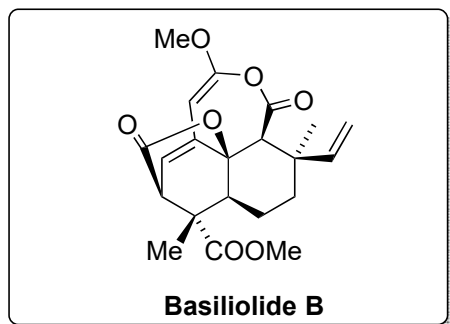




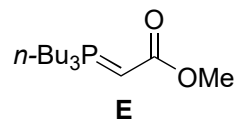
↓
10-15



↓
16+17



- 10) VO(acac)₂, TBHP
- 11) Ag₂O, MeI
- 12) **E**, toluene, 100 °C
- 13) CrO₃, H₂SO₄
- 14) DABCO, toluene, 70 °C
- 15) 120 °C, toluene, sealed tube



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

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

- 16) Pd(PPh₃)₄, PPh₃
- 17) Tf₂O, Et₃N, pyrrolidine

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?

