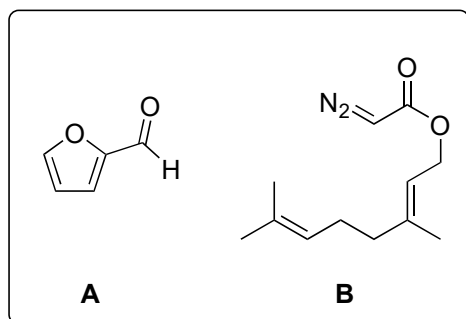


Diastereoselective Total Synthesis of (±)-Basiliolide B

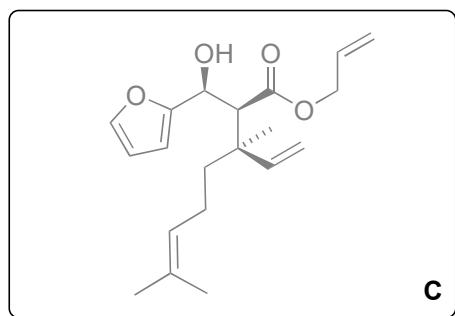
X. Liang, L. Zhou, L. Min, W. Ye, W. Bao, W. Ma, Q. Yang, F. Qiao, X. Zhang, and C.-S. Lee

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

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

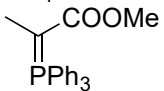


1–6

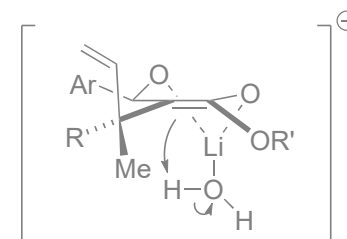


7–9

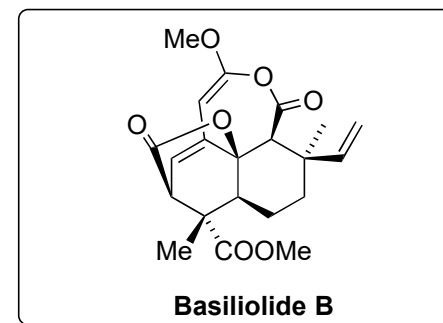
- 1) DBU, IBX, DMSO
- 2) $\text{Cu}(\text{TBS})_2$, toluene, 80 °C
- 3) NaBH_4
- 4) KOH, EtOH, *then* allylBr
- 5) PPh_3 , I_2 , imidazole
- 6) *n*-BuLi, THF, -80 °C, 15 min

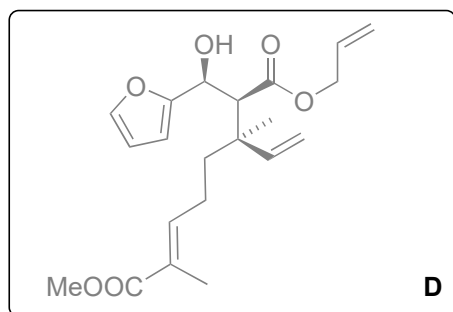
- 7) *m*-CPBA
- 8) NaIO_4
- 9) 

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

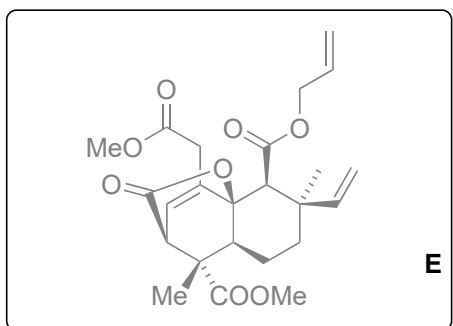


Mohrig's chelation model *JACS* **2011**, *133*, 5124–5128.

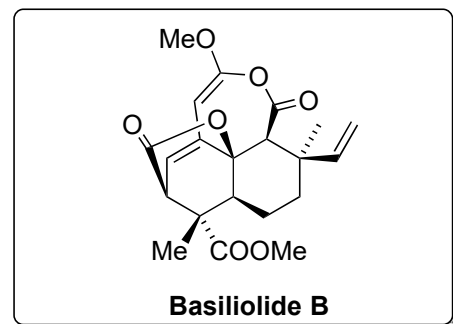




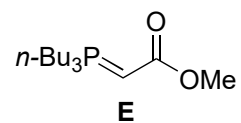
10-15



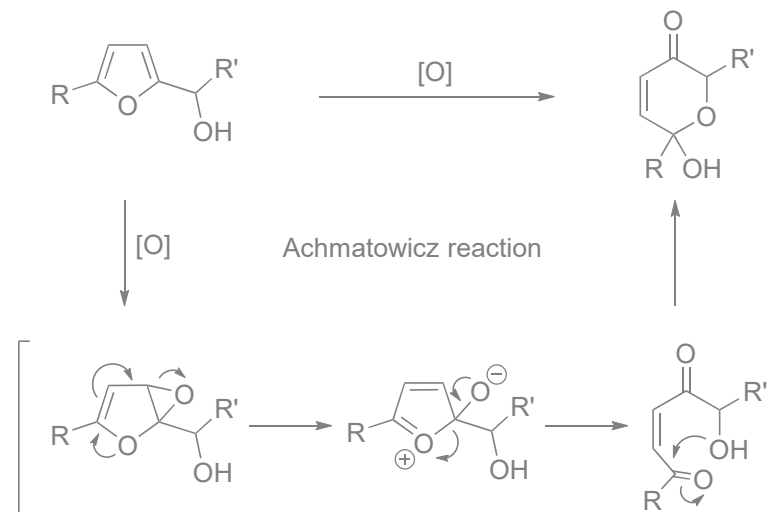
16+17



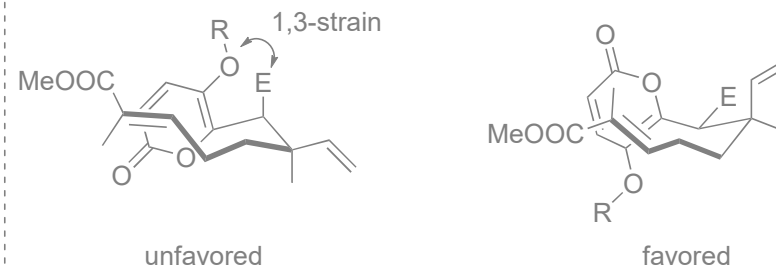
- 10) VO(acac)₂, TBHP
- 11) Ag₂O, MeI
- 12) **E**, toluene, 100 °C
- 13) CrO₃, H₂SO₄
- 14) DABCO, toluene, 70 °C
- 15) 120 °C, toluene, sealed tube



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

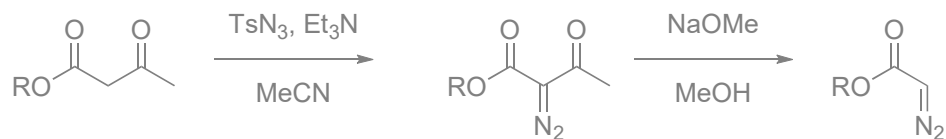


Please provide two possible transition states which explain the diastereoselectivity of step 15.



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

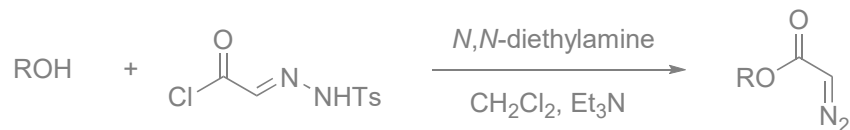
Regitz:



Fukuyama:

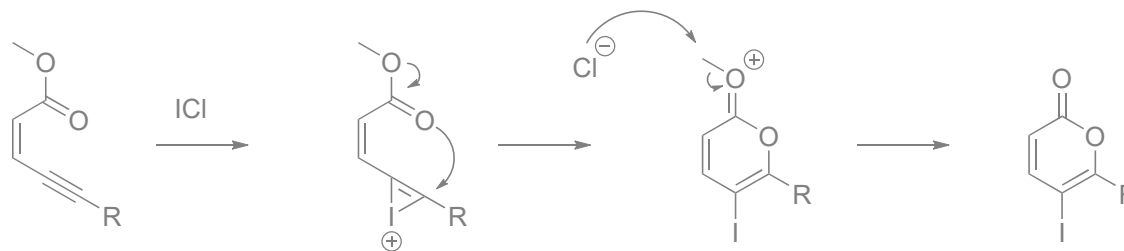


House:

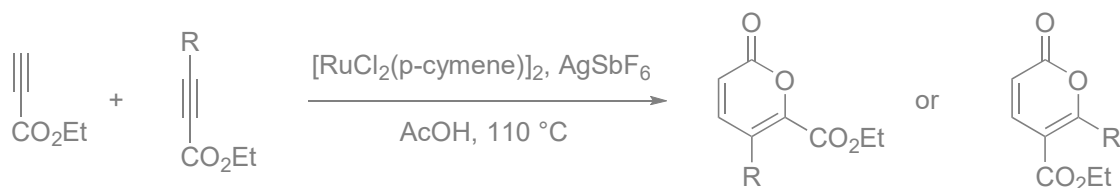
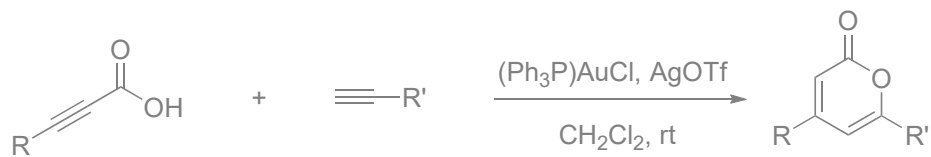


The Dudley and the Stoltz group used a different approach to furnish the alpha-pyrone. Please name the reaction and come up with a mechanism. Which other methods for the synthesis of alpha-pyrones do you know?

Rossi-Larock iodo cyclization:



two other examples:



pK_A values of mentioned bases:

DBU	12
<i>n</i> -BuLi	50
DABCO	9
Et_3N	11