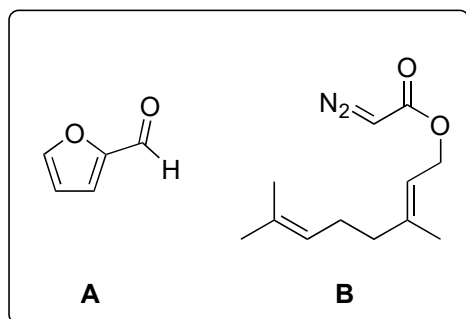


## Diastereoselective Total Synthesis of (±)-Basiliolide B

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

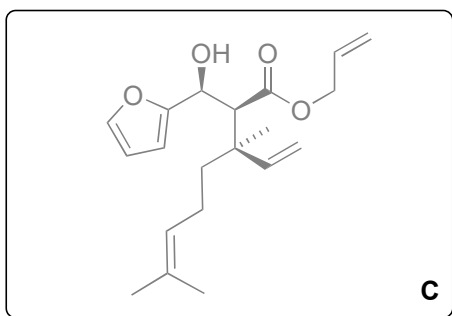
*Angew. Chem. Int. Ed.* **2014**, *53*, 11294–11297.

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

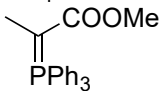


1–6

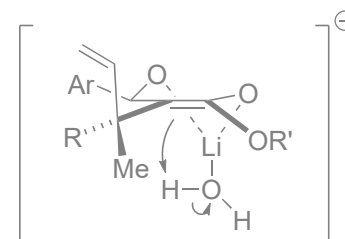
- 1) DBU, IBX, DMSO
- 2)  $\text{Cu}(\text{TBS})_2$ , toluene, 80 °C
- 3)  $\text{NaBH}_4$
- 4) KOH, EtOH, *then* allylBr
- 5)  $\text{PPh}_3$ ,  $\text{I}_2$ , imidazole
- 6) *n*-BuLi, THF, -80 °C, 15 min



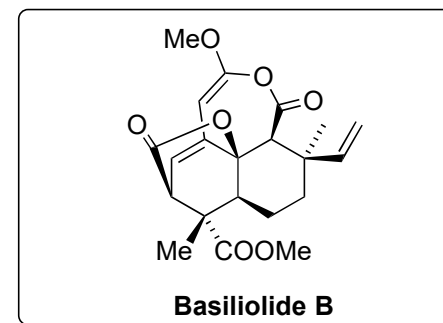
7–9

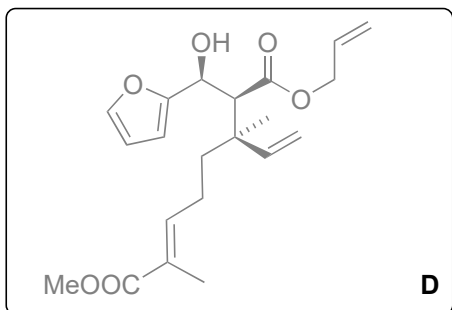
- 7) *m*-CPBA
- 8)  $\text{NaIO}_4$
- 9) 

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

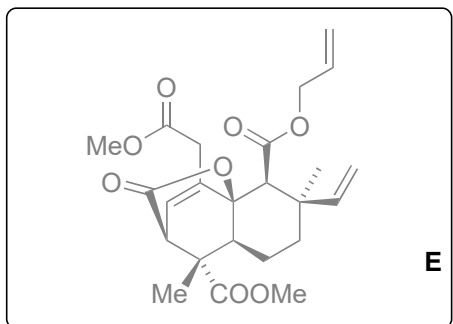


Mohrig's chelation model *JACS* **2011**, *133*, 5124–5128.

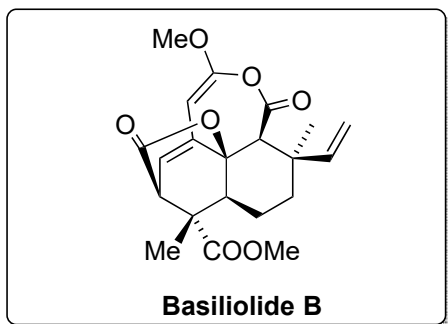




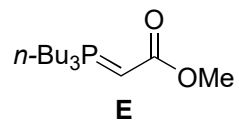
10-15



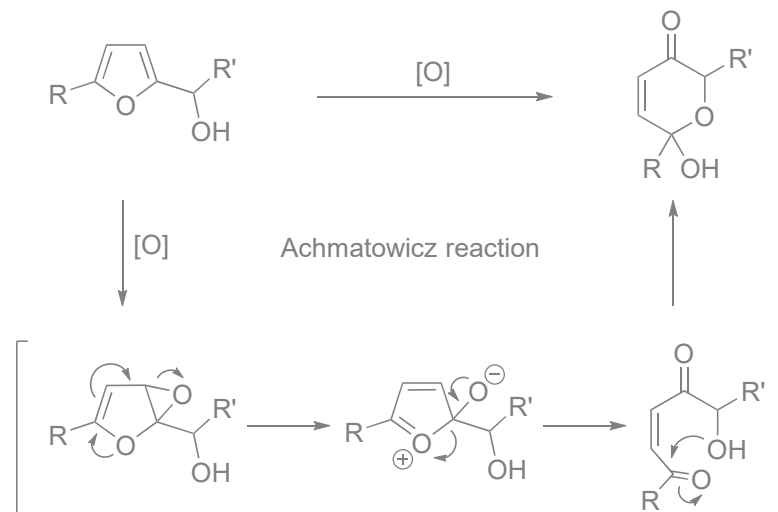
16+17



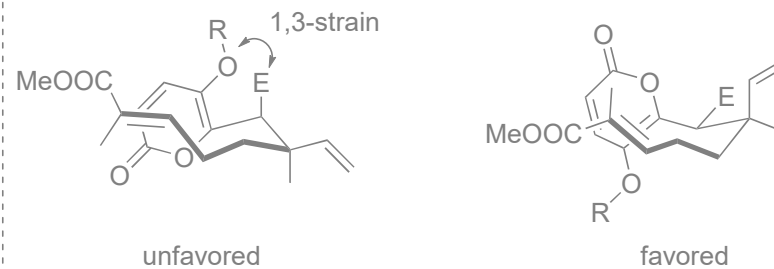
- 10) VO(acac)<sub>2</sub>, TBHP
- 11) Ag<sub>2</sub>O, MeI
- 12) **E**, toluene, 100 °C
- 13) CrO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>
- 14) DABCO, toluene, 70 °C
- 15) 120 °C, toluene, sealed tube



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

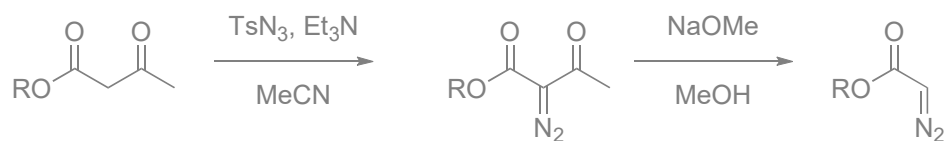


Please provide two possible transition states which explain the diastereoselectivity of step 15.



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

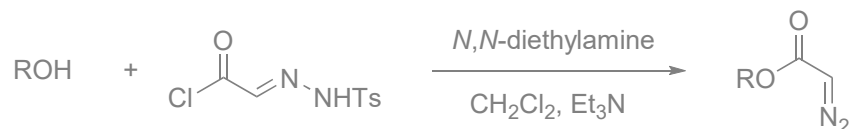
Regitz:



Fukuyama:

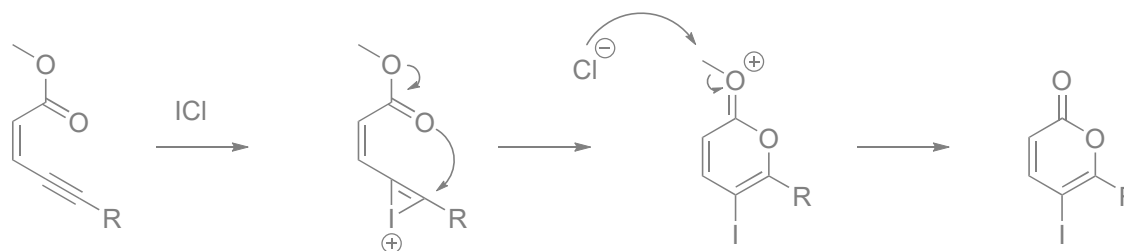


House:



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-pyrone do you know?

Rossi-Larock iodo cyclization:



two other examples:

