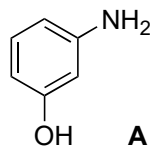
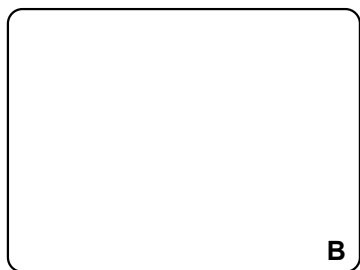


Total Syntheses of (+)- and (-)-Tetrapetalones A and C

Dhanjee, H. H.; Kobayashi, Y.; Buergler, J. F.; McMahon, T. C.; Haley, M. W.; Howell, J. M.; Fujiwara, K.; Wood, J. L.
J. Am. Chem. Soc. **2017**, *139*, 14901–14904



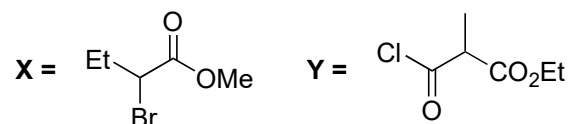
1–3



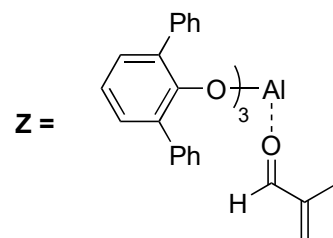
4–6



7–9



- 1) **X**, Δ
- 2) TIPSCl, imidazole *then* **Y**, DMAP
- 3) DBU, 4 Å MS, Δ



- 4) NaHMDS, **Z** *then* Br₂
- 5) NaClO₂, H₂O₂, NaH₂PO₄
- 6) (COCl)₂, DMF (cat.) *then* HFIP, μ W *then* DBU, TIPSCl

- 7) Pd(TFA)₂, Δ , PIFA, *then* SiO₂
- 8) CeCl₃, NaBH₄
- 9) BF₃•OEt₂ *then* *trans*-crotyl silane

Hint: B is a mixture of diastereomers

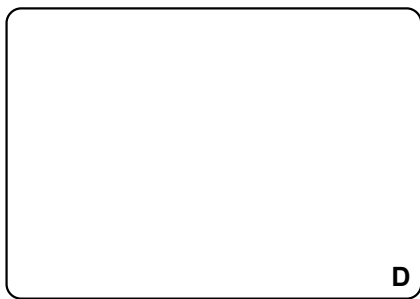
Please provide name of the reaction in **Step 5**.

Hint: C is obtained with a *dr* of 2.8:1 and then purified. Draw the one important stereocenter product-like.

Please provide name of the reaction in **Step 6** (second part) and the mechanism to **C**.

Hint: Several transformations take place

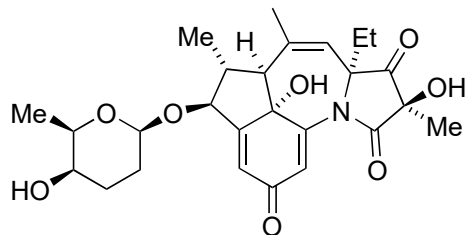
Please provide a mechanism for **Step 7** and **9**.



10–14

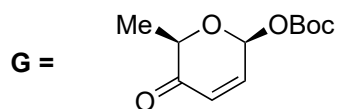


15–20

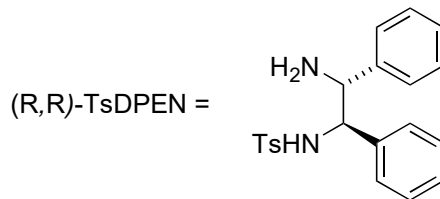


(-)-tetrapetalone C

- 10) Tf_2O , pyridine
- 11) $\text{Pd}(\text{PPh}_3)_4$ (cat.), Et_3N , μW
- 12) DMDO
- 13) NaIO_4 , Δ
- 14) CeCl_3 , NaBH_4



- 15) **G**, $\text{Pd}(\text{PPh}_3)_4$ (cat.), 4 Å MS
- 16) $[\text{Cp}^*\text{RhCl}_2]_2$, (*R,R*)-TsDPEN, NaHCO_2 , $\text{THF}:\text{H}_2\text{O}$
- 17) TBAF (*t*-BuOH)₄
- 18) PIDA, *t*-BuOOH
- 19) Pb/Cd
- 20) LiOMe
- 21) DMDO



Hint: Step 15 gives a 1:1 mixture of diastereomers which can be resolved towards the natural and unnatural enantiomer of the final product.

Hint: Step 18 and **19** are best approached together.