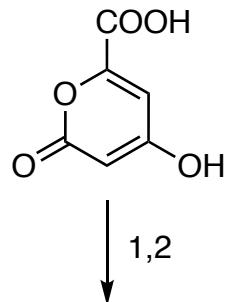


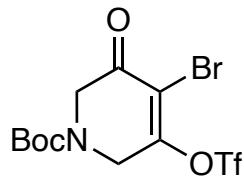
Total synthesis of lissodendoric acid A via stereospecific trapping of a strained cyclic allene

Ippoliti, F. M.; Adamson, N. J.; Wonilowicz, L. G.; Nasrallah, D. J.; Darzi, E. R.; Donaldson, J. S.; Garg, N.K.

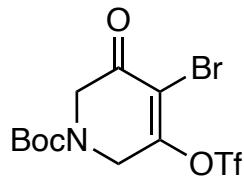
Science 2023, 379, 261-265



1,2

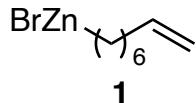


3-6



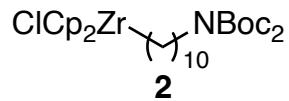
B

- 1) TsCl (excess), TEA, DCM *then* *t*-BuOH, 40 °C
2) **1**, PdCl₂(PPh₃)₂ (20 mol%), NMI, DMA



- 2) What type of cross-coupling is this reaction?

- 3) **2**, CuBr•SMe₂, THF, 40 °C
4) (*R*)-CBS cat. (20 mol%), BH₃•SMe₂, THF, 30 °C
5) EtOC(O)Cl, pyr., DCM
6) PhMe₂SiLi, CuCN, PPh₃, Et₂O/THF, -78 °C



Lissodendoric Acid A

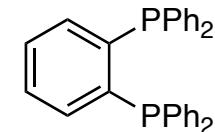
7-14



- 7) **A**, CsF , $n\text{-Bu}_4\text{NBr}$, MeCN , -20°C
- 8) PDC, $t\text{-BuOOH}$, PhH
- 9) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, BDP (50 mol%), PMHS, $t\text{-BuOH}$, PhMe
- 10) MeCN , 80°C then $\text{Cu}(\text{OTf})_2$ (20 mol%), 40°C
- 11) acryloyl chloride, TEA, DCM
- 12) Grubbs's II (20 mol%), DCM, 40°C
- 13) $\text{Rh}(\text{cod})(\text{acac})$ (50 mol%), PhSiH_3 , DCM, 40°C
- 14) TFA, DCM, -78°C to 23°C

7) Rationalize the regiochemical outcome of this reaction.

9) Structure of BDP:



10) Hint: 3 eq. CO_2 are liberated throughout this two-part transformation.