Synthesis of (–)-Picrotoxinin by Late-Stage Strong Bond Activation

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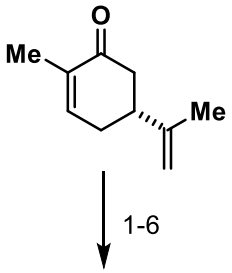

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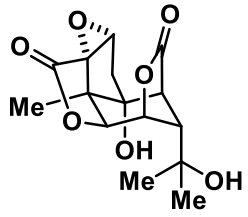
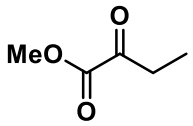


(–)-Picrotin

1. LDA, MeI, THF, –78 → 0 °C
2. LDA, MeI, THF, –78 → 0 °C
3. NaHMDS, $MgCl_2$, **1**, THF –78 → 0 °C
4. $SOCl_2$, pyr, DMAP, MeCN, 50 °C
5. LDA, THF, 0 → 23 °
6. NBS, THF, 0 °C



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7. *m*–CPBA, $KHCO_3$, DCM, H_2O
8. OsO_4, NMO, citric acid, *t*-BuOH, H_2O, 7 days
9. AgOAc, I_2, hν, DCM
10. TFDO, $NaHCO_3$, $MeCOCF_3$, 0 °C
11. AgOAc, I_2, hν, DCM
12. AIBN, Bu_3SnH, PhMe, 85 °C *then* $NaHCO_3$,MeOH 0 °C
13. $Pb(OAc)_4$, I_2, $CaCO_3$, PhH, hν
14. Zn, NH_4Cl, EtOH, 95 °C
15. $Co(acac)_2$, $PhSiH_3$, O_2, *i*-PrOH

Step 1: Name the starting material

Hint steps 1 and 2: Not a mistake

Hint step 8: 2 transformations

Step 9: Name of the reaction?

Step 10: How would you prepare TFDO?

Step 12: Structure of AIBN?

Step 15: Name of the reaction?