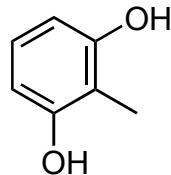


The Total Synthesis of (\pm)-11-O-Debenzoyltashironin

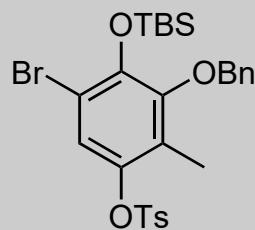
Cook, S. P.; Polara, A.; Danishefsky, S. J.

J. Am. Chem. Soc. 2006, 128, 16440–16441.

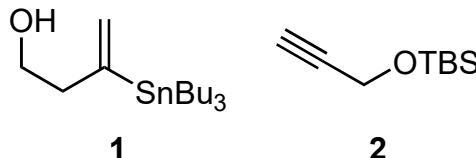


1-6

- 1) $Zn(CN)_2$, HCl
- 2) $TsCl$, -10 °C
- 3) $BnBr$, K_2CO_3 , TBAI
- 4) *m*-CBPA *then* NEt_3 , MeOH/ CH_2Cl_2
- 5) NBS
- 6) $TBSCl$, NEt_3



A



1

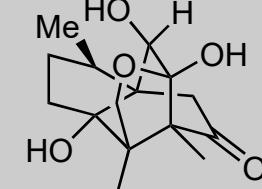
2

7-12

- 7) 1, $Pd(dba)_3$, $P(t-Bu)_3$
- 8) DMP
- 9) 2, Et_2Zn , *then* $Ti(OiPr)_4$, substrate
- 10) $MsCl$, NEt_3 *then* $Me_2Cu(CN)Li_2$
- 11) TBAF, AcOH
- 12) PIDA *then* μW

1) Name the reaction, draw active species, hint: formylation

4) Name the first transformation

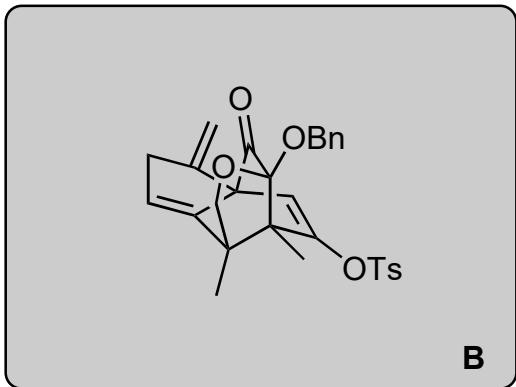


(\pm)-11-O-Debenzoyltashironin

9) What is formed in the first transformation?

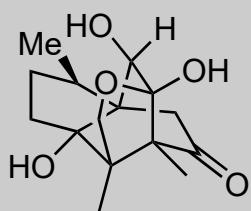
11) hint: double deprotection

12) Draw the mechanism, hint: at first a macrocycle is formed



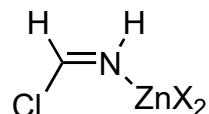
13-20

- 13) NaBH_4
- 14) TMS-imidazole
- 15) *m*-CBPA
- 16) $(\text{PPh}_3)_3\text{RhCl}, \text{H}_2$
- 17) LiEt_3BH (52 eq)
- 18) DMP
- 19) Hf-pyr, TBAF
- 20) H_2 , Pd/C



(\pm)-11-O-Debenzoyltashironin

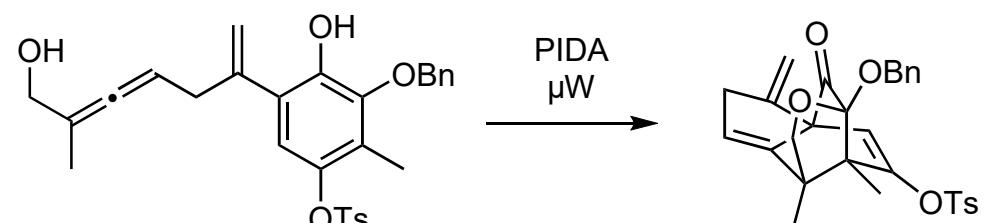
solution to
step 1: Gattermann reaction



step 4: Baeyer–Villiger Oxidation

step 9:

step 12:



PIDA
↓

