Concise and Stereoselective Synthesis of Annotinolides C, D, and E

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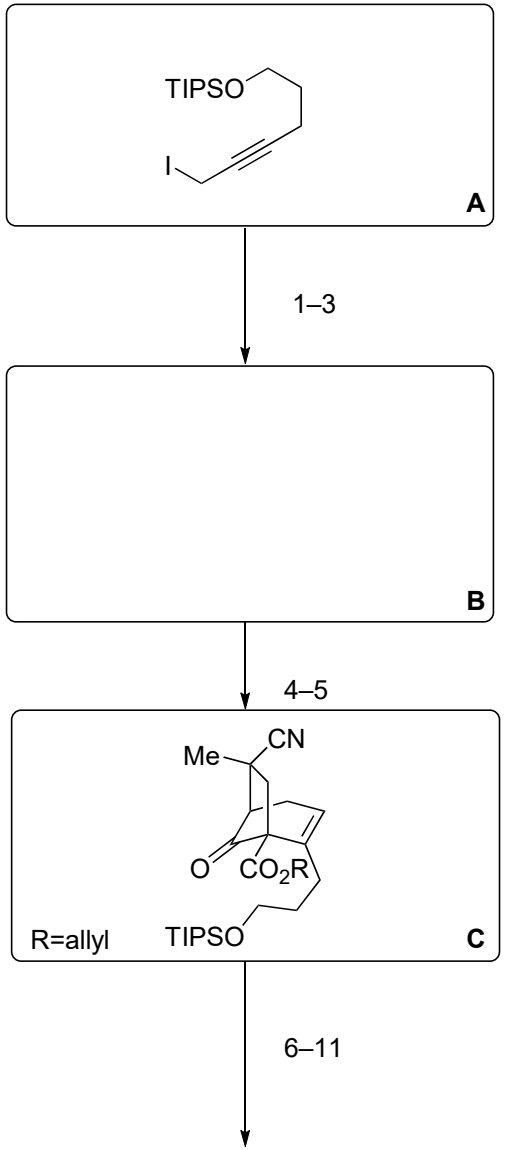
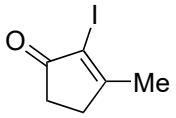
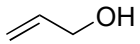




1

1) **1**, *i*-PrMgCl, *then* CuCN•2LiCl, *then* **A**
2) Et_3Al, TMSCN, *then* HCl
3) LDA, $NCCO_2Me$

2) Name of reagent, which is generated *in situ*?
3) Name of reagent?

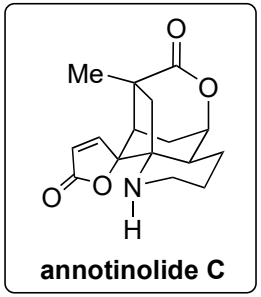
4) TBSOTf, 

5) JohnPhosAu-(NCMe)SbF_6

5) Hint: Key cyclization step.

6) $CeCl_3$, $NaBH_4$
7) TBSOTf, 2,6-lutidine
8) $Pd(PPh_3)_4$, pyrrolidine
9) DPPA, Et_3N, *t*-BuOK
10) DIBAL-H
11) $NaClO_2$

9) Name of reaction?



annotinolide C

R=Boc **D**

12–15

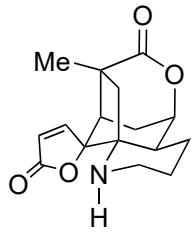
12) NIS
13) TBAF
14) *n*-Bu_3SnH, Et_3B, air
15) Dess–Martin periodinane

13) Hint: Only one protecting group is removed.

R=Boc **E**

16–19

16) Li—≡—CO_2Me
17) H_2, Pd/C, quinoline, *then* silica gel
18) TBAF
19) MsCl, Et_3N, *then* TFA, *then* $NaHCO_3$



annotinolide C