An Efficient Synthetic Approach to Cyanocycline A and Bioxalomycin β2 via [C+NC+CC] Coupling

P. Garner, Ü. Kaniskan, C. M. Keyari, L. Weerasinghe *J. Org. Chem.* **2011**, *76*, 5283–5294.
Ü. Kaniskan, P. Garner *J. Am. Chem. Soc.* **2007**, *129*, 15460–15461.

Boc-D-Serine

↓ 1–4

1) MeI, $NaHCO_3$
2) TsOH, $Me_2C(OMe)_2$
3) DIBAL-H
4) BnNHOH, $MgSO_4$

A

Oppolzer's L-*camphorsultam*

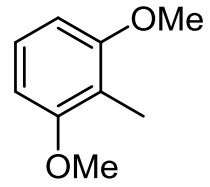
↓ 5–6

5) *n*-BuLi, bromoacetyl bromide
6) urotropine, *then* conc. HCl

How would you prepare Oppolzer's sultam? (hint: start from CSA!)

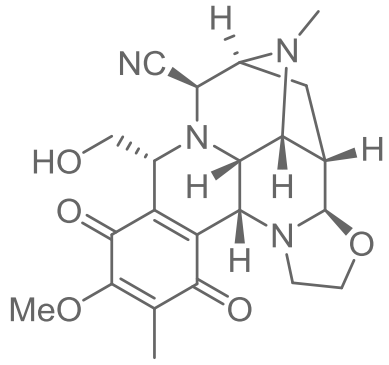
step 6: name of reaction?

B

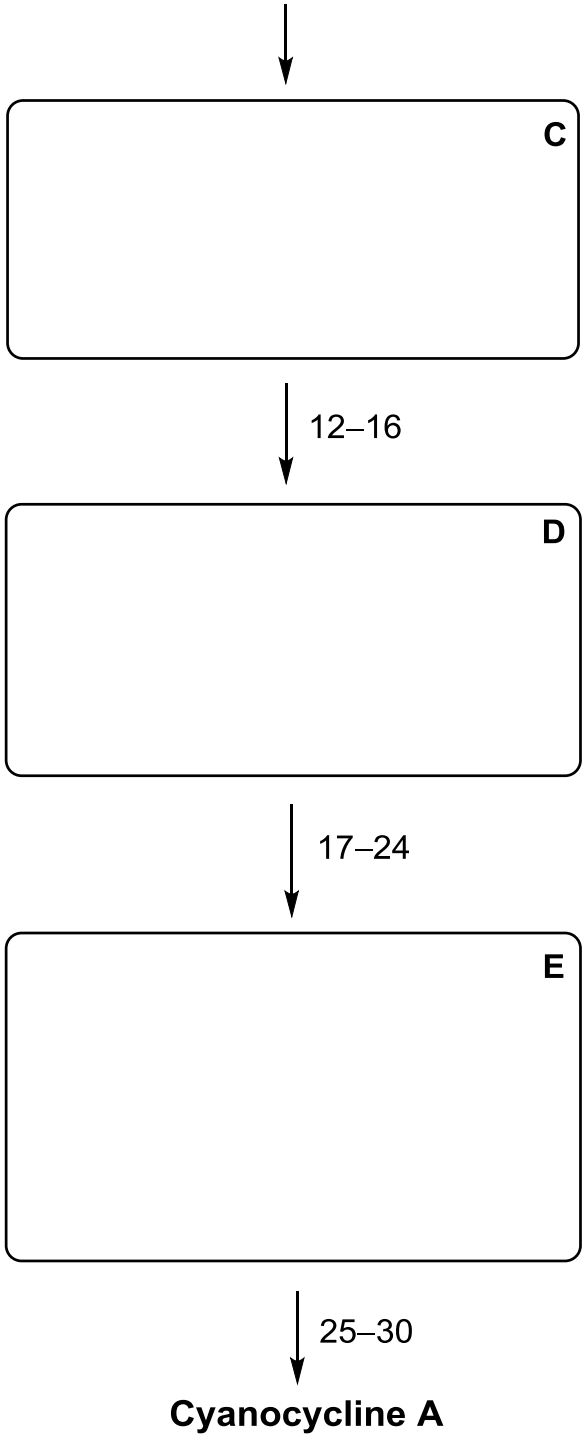


↓ 7–11

7) EtCOCl, $TiCl_4$
8) *m*-CPBA
9) NBS
10) KOH, MeOH
11) BnBr, NaH



Cyanocycline A



12) Mg, $(CH_2Br)_2$, **A**
13) Zn, NH_4OH
14) CbzCl, $NaHCO_3$
15) TsOH, MeOH
16) DMP

17) AgOAc, CH_2CHCO_2Me, **B**
18) Pd/C, H_2
19) CbzCl, DIPEA
20) TFA
21) $BnOCH_2CHO$, AcOH, 4Å MS
22) BnBr, K_2CO_3
23) LAH
24) DMSO, NEt_3, $(COCl)_2$

25) TMSCN; $ZnCl_2$
26) Lawesson's Reagent
27) Ra-Ni
28) oxirane, MeOH, 60 °C
29) BCl_3
30) $Mn(OAc)_3$

Step 12: Please explain the stereochemical outcome of this reaction (transition state!)

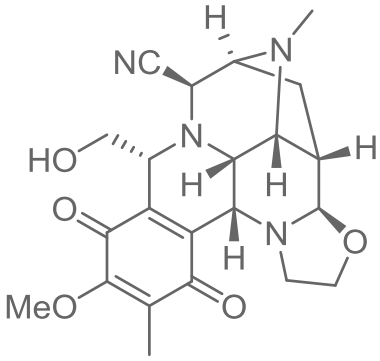
Step 17: Come up with a mechanism that explains the reaction's stereoselectivity

Step 21: name of reaction ?

Hint: two positions get reduced in Step 23

Step 26: Structure of L.R. and how would you prepare it?

Hint (Step 27): position of interest does not get completely reduced



Cyanocycline A