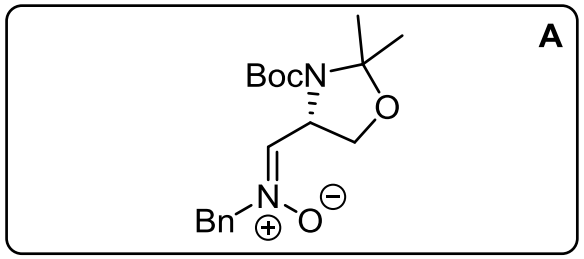
An Efficient Synthetic Approach to Cyanocycline A and Bioxalomycin β2 via [C+NC+CC] Coupling

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

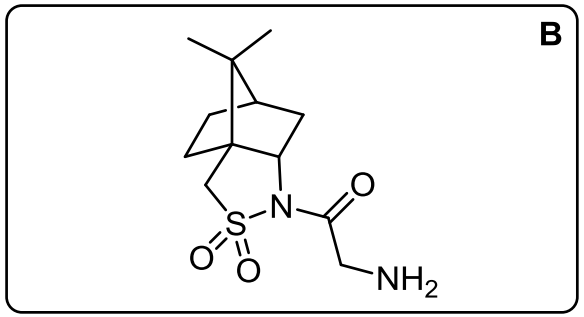
1–4



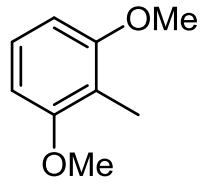
1) MeI, $NaHCO_3$
2) TsOH, $Me_2C(OMe)_2$
3) DIBAL-H
4) BnNHOH, $MgSO_4$

Oppolzer's **L**-*camphorsultam*

5–6



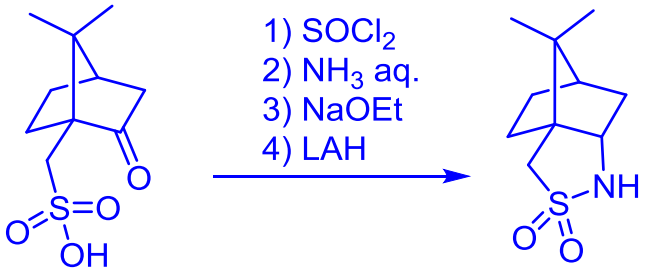
5) *n*-BuLi, bromoacetyl bromide
6) urotropine, *then* conc. HCl



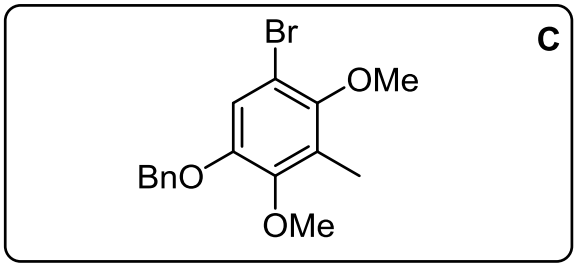
7–11

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

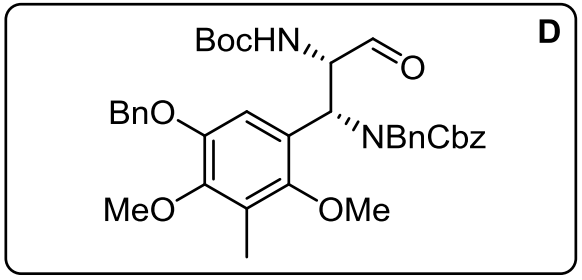
How would you prepare Oppolzer's sultam? (hint: start from CSA!)



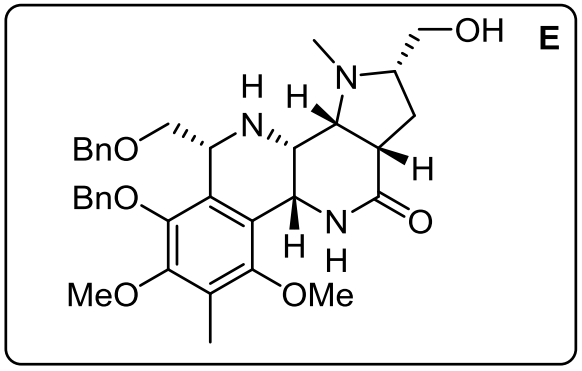
step 6: name of reaction?
→ *Délepine Reaction*



12–16



17–24



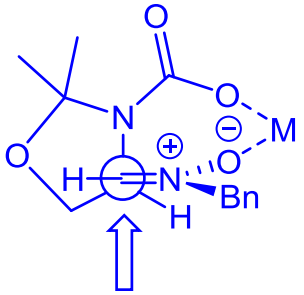
25–30

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) $Mn(OAc)_3$

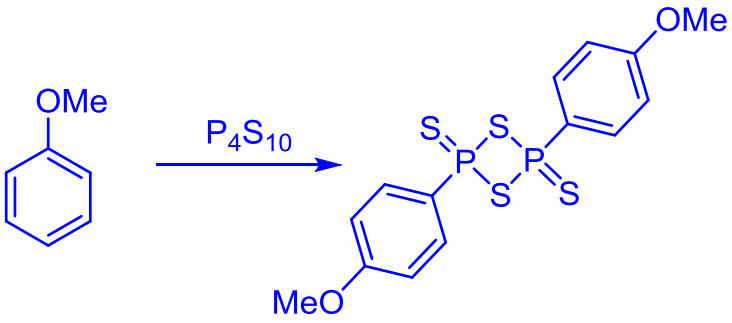
Step 12: Please explain the stereochemical outcome of this reaction (transition state!)

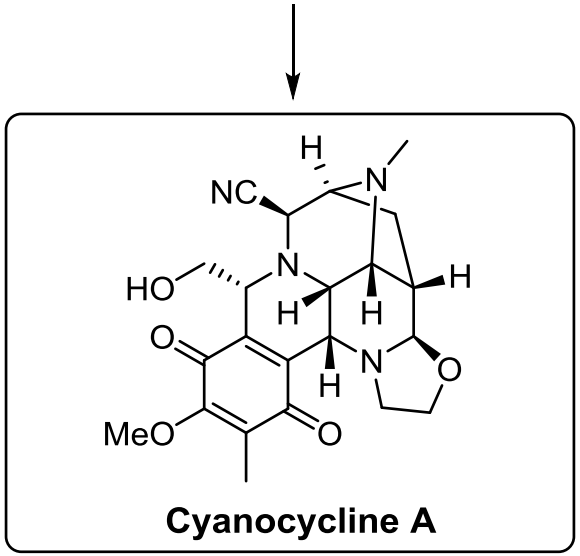


re-attack

Step 21: name of reaction ?
Pictet-Spengler Reaction

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





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