Total Synthesis of (−)-Chromodorolide B


How would you synthesize bicycle A?

Please come up with a mechanism for step 4.

1) ethylene glycol, p-TsOH
2) LiAlH₄
3) MeOOCOCI, DMAP
4) Pd(acac)₂, Bu₃P, HCO₂H
5) Et₂Zn, ClCH₂I, CH₂Cl₂
   then HCl, MeOH
6) H₂, PtO₂, AcOH
7) PCC, CH₂Cl₂
8) NH₂NH₂, EtOH
9) I₂, TMG, THF
10) aldehyde C, CrCl₂, NiCl₂,
    ligand L, Et₃N, THF
11) KOH, 50 °C
12) PhthNOH, DCC
13) SOCl₂, pyridine

Name reaction of step 10?

14) Ru(bpy)₃(PF₆)₂ (1 mol%), butenolide E
d₂-HE, blue LED, MeCN, rt, 6H

How would you prepare aldehyde C?

Please provide a mechanism for step 14.

Two different products F and G were here obtained. Neglect stereochemistry (They also isolated an epimer for each F and G). Think about the use of d₂-HE instead of undeuterated Hantzsch ester.
15) DIBAL-H, \(-78^\circ C, 2h\), then \(\text{Ac}_2\text{O}, \text{DMAP}, \text{pyridine}\)
16) \(\text{HCO}_2\text{H}, \text{Pd/C}\)
17) \(\text{H}_2, \text{PtO}_2\)
18) DMP
19) \(\text{NaClO}_2, 2\text{-methyl-2-butene, NaH}_2\text{PO}_4\)
20) 4M HCl, THF
21) \(\text{Ac}_2\text{O}, \text{pyridine, DMAP}\)

\((-\text{-Chromodorolide B})\)