Asymmetric Total Synthesis of Illisimonin A

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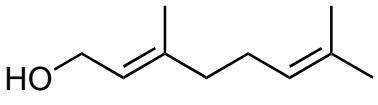
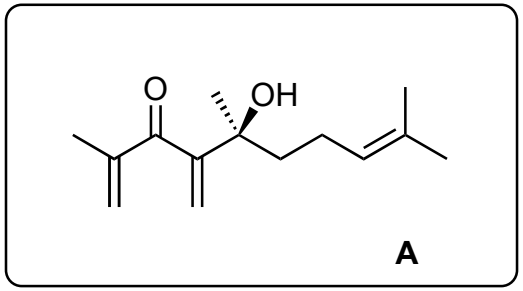


1-9



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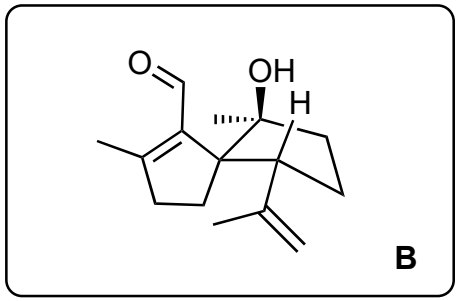
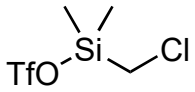


1) $Ti(OiPr)_4$, *t*BuOOH, L-(+)-diisopropyl tartrate
2) CCl_3CN, PPh_3
3) *n*BuLi
4) $Zn(CN)_2$, $Ni(acac)_2$, neocuproine, Mn
5) TESOTf, 2,6-lutidine
6) DIBAL
7) 2-bromopropene, *t*BuLi
8) TBAF
9) IBX

10) $B(C_6F_5)_3$ *then* TESOTf, 2,6-lutidine
11) KHMDS *then* $P(OEt)_3$, O_2
12) **1**, 2,6-lutidine
13) LDA
14) MeMgCl
15) $HClO_4$

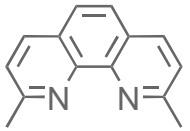


1

1) Name of starting material?

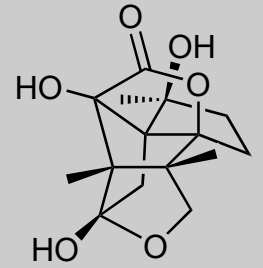
geraniol

4) Structure of neocuproine?



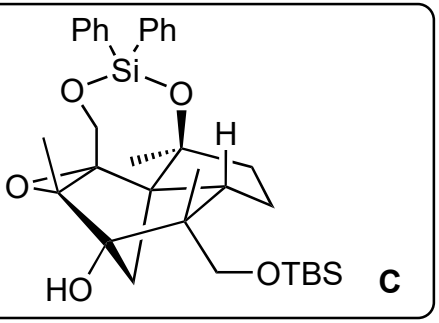
10) *Hint: 2 rings formed.* Please show mechanism and suggest name.

tandem Nazarov-ene cyclization (see later)



illisimonin A

16-22



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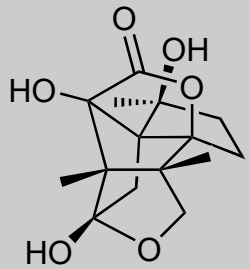
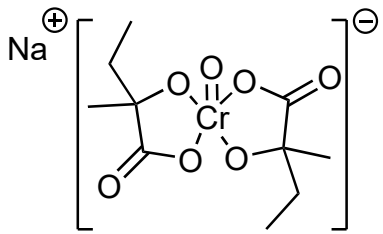
23-28



illisimonin A

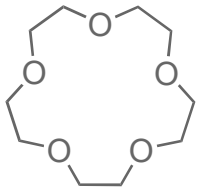
16) DIBAL
17) Ph_2SiCl_2, DMAP, Et_3N
18) **2**, 15-crown-5
19) *m*CPBA, $NaHCO_3$
20) Cp_2TiCl_2, Zn
21) TBSCl, imidazole
22) *m*CPBA, $NaHCO_3$



2

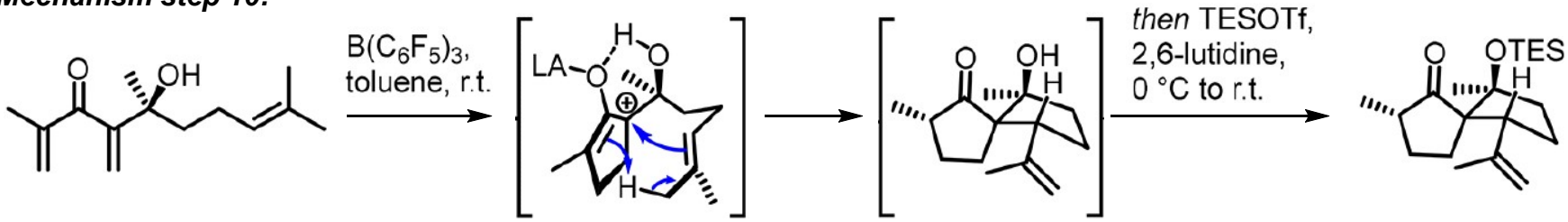
23) $SnCl_4$
24) HF
25) IBX
26) $NaClO_2$, NaH_2PO_4, 2-methyl-2-butene
27) AcCl
28) Fe(PDP), H_2O_2

18) Structure of 15-crown-5?



23) Name of the reaction? Please suggest a mechanism.
semipinacol rearrangement (see later)
26) Name of the reaction?
Pinnick oxidation
28) Name of the reaction?
White–Chen oxidation

Mechanism step 10:



Mechanism step 23: