# Asymmetric Total Synthesis of Shizukaol J, Trichloranoid C and Trishizukaol A

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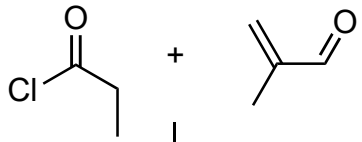


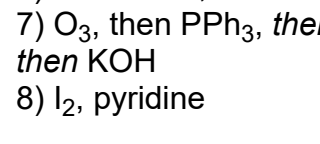

1–8

**A**

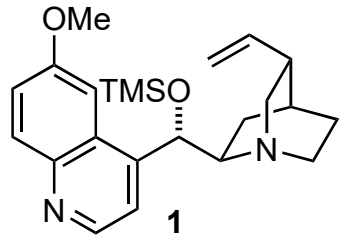
9–11

**B**

1) **1**, LiI, *i*-$Pr_2NEt$
2) LiHMDS (5.5 eq) , allyl iodide, HMPA, *then t*-BuOAc, *then* $HCl_{aq}$ (5.5 eq), *then* $NaBH_4$
3) *p*-TsOH•$H_2O$
4) $SOMe_3I$, NaH
5) MeLi
6) Grubbs$^{2nd}$, *then* MOMCl, *i*-$Pr_2NEt$, TBAI
7) $O_3$, then $PPh_3$, *then* piperidine, AcOH, *then* KOH
8) $I_2$, pyridine




**2**

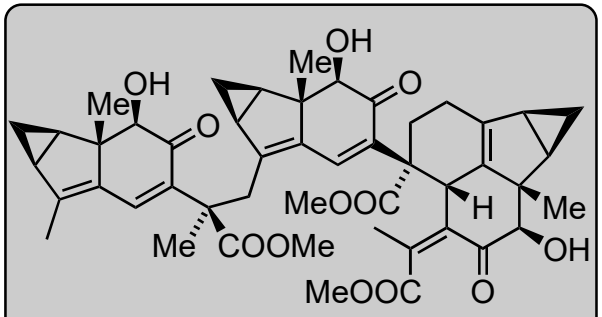



**1**

9) **2**, CuI, CsF, $Pd(PPh_3)_4$
10) DBU, 130 °C
11) TMSCl

1) Propose a mechanism

3) Hint: two reactions take place
4) Name?




**trishizukaol A**

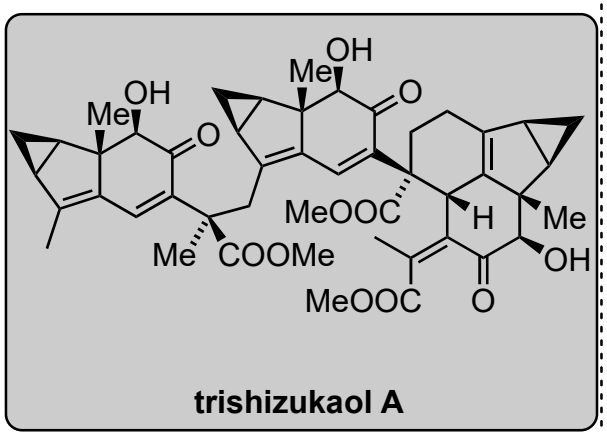
**A**

9`–11`

**C**

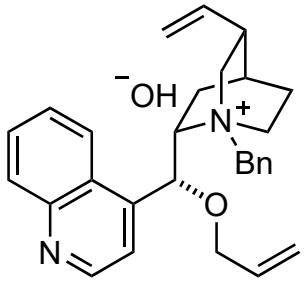
**B + C**

12–18

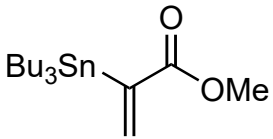



**trishizukaol A**

9`) $SeO_2$
10`) $LiAlH(Ot\text{-}Bu)_3$
11`) $CBr_4$, $PPh_3$, imidazole

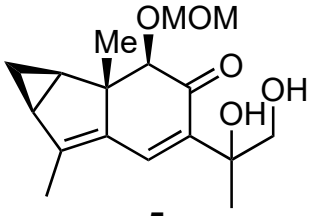



**3**




**4**

12) **3**, CsOH, $MnSO_4$, $H_2O$, toluene
13) $NaClO_2$, $NaH_2PO_4$, isopentene, *t*-BuOH *then* $TMSCHN_2$
14) **4**, CuI, CsF, $Pd(PPh_3)_4$
15) **5**, PhCOOH, 170 °C
16) $O_2$, methylene blue, h$\nu$, HCl, MeOH
17) KOH
18) $TMSCHN_2$, MeOH




**5**

9`) Name?

11`) Name?

12) What is the role of **3**?
13) Name?

14) Name?
15) Hint: 2 rings are formed
16) Hint: 4 reactions occur