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

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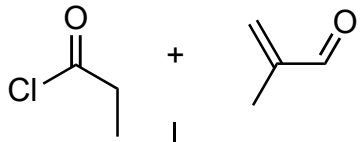

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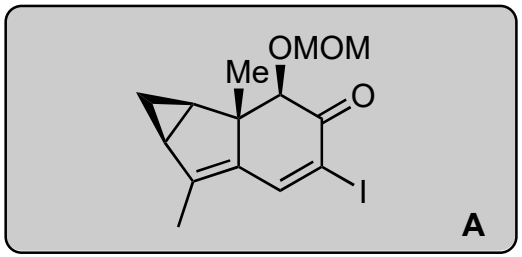

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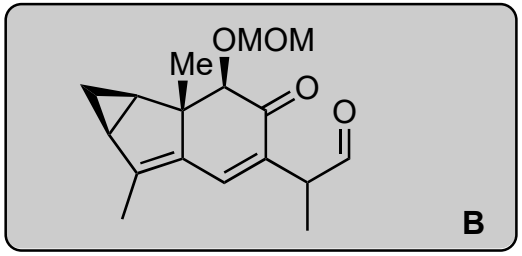
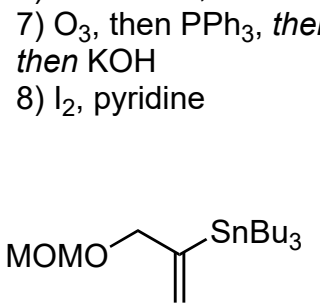


1) **1**, LiI, *i*-Pr_2NEt
2) LiHMDS (5.5 eq) , allyl iodide, HMPA, *then t*-BuOAc, *then* HCl_{aq} (5.5 eq), *then* $NaBH_4$
3) *p*-TsOH•H_2O
4) $SOMe_3I$, NaH
5) MeLi
6) Grubbs^{2nd}, *then* MOMCl, *i*-Pr_2NEt, TBAI
7) O_3, then PPh_3, *then* piperidine, AcOH, *then* KOH
8) I_2, pyridine



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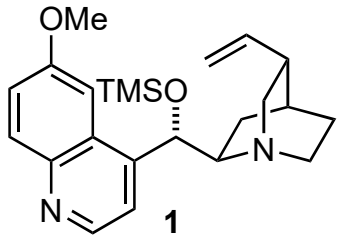
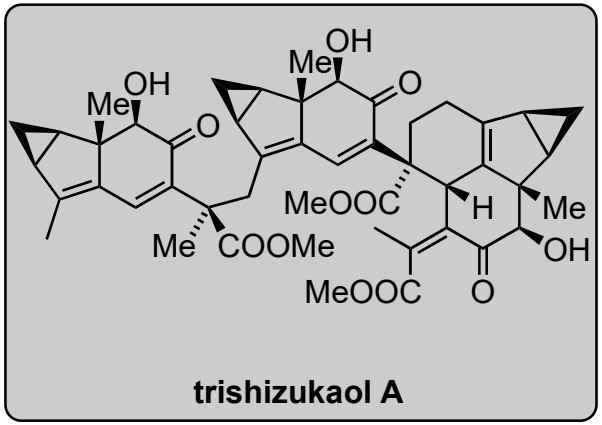


1

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

1) Propose a mechanism

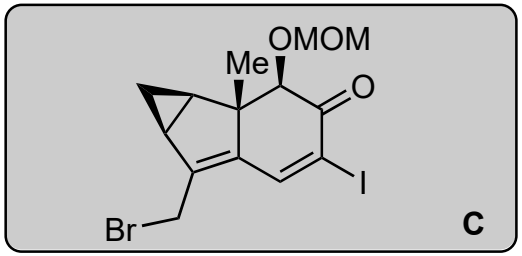
3) Hint: two reactions take place
4) Name? Corey–Chaykovsky cyclopropanation



trishizukaol A

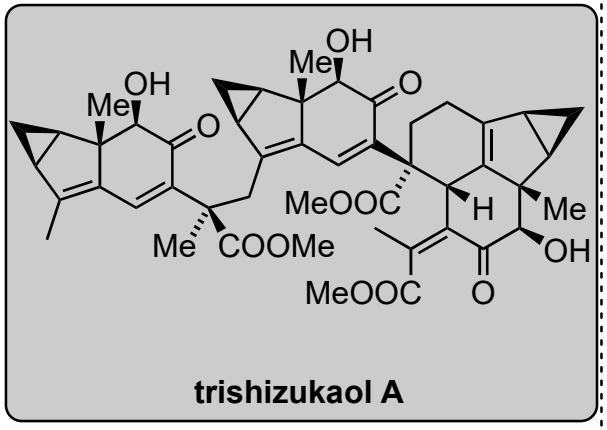
A

9`–11`

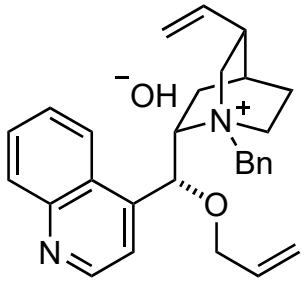


B + C

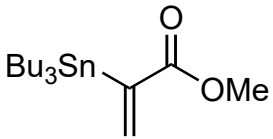
12–18



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

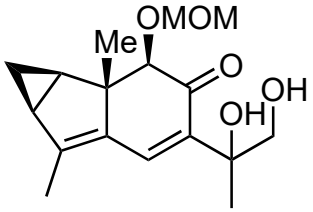


3



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, hν, HCl, MeOH
17) KOH
18) $TMSCHN_2$, MeOH



5

9`) Name? Riley oxidation

11`) Name? Appel reaction

12) What is the role of **3**? chiral phase transfer catalyst
13) Name? Pinnick–Kraus oxidation
14) Name? Stille coupling
15) Hint: 2 rings are formed
16) Hint: 4 reactions occur

Key for 1): *J. Am. Chem. Soc.* **2004,** *126*, 5352.