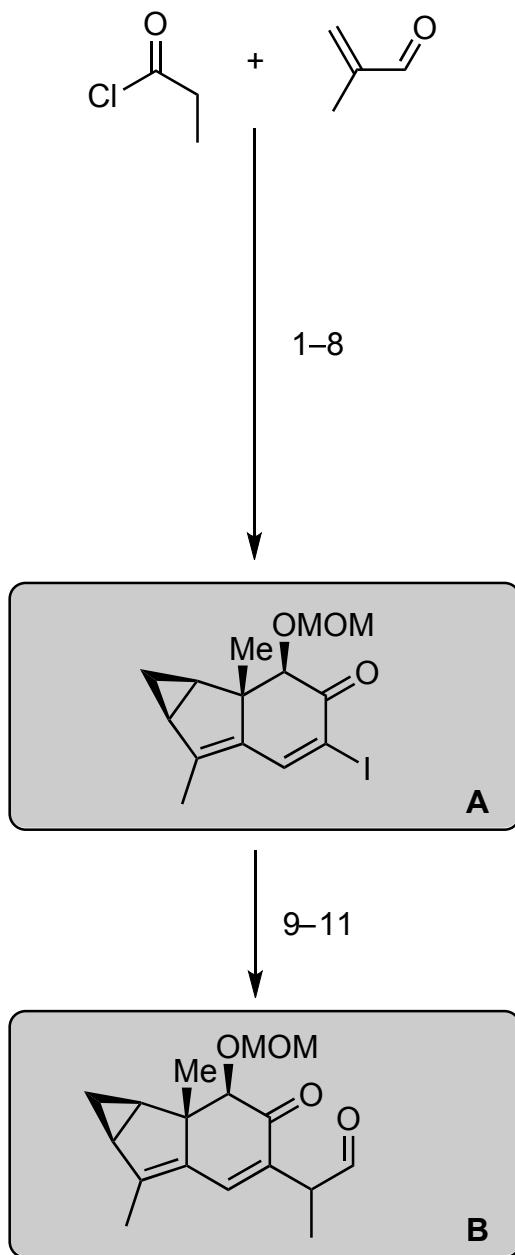
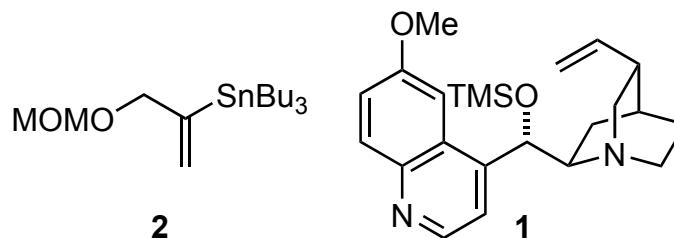


Asymmetric Total Synthesis of Shizukaol J, Trichloranoid C and Trishizukaol A

Wang, X; Wang, Z; Ma, X; Huang, Z; Sun, K; Gao, X; Fu, S; Liu, B*. *Angew. Chem. Int. Ed.* **2022**, 10.1002/anie.202200258.

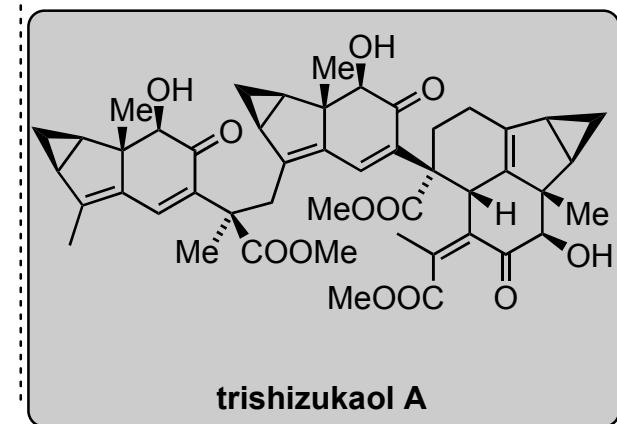


- 1) **1**, LiI, *i*-Pr₂NEt
- 2) LiHMDS (5.5 eq), allyl iodide, HMPA, *then* *t*-BuOAc, *then* HCl_{aq} (5.5 eq), *then* NaBH₄
- 3) *p*-TsOH•H₂O
- 4) SOMe₃I, NaH
- 5) MeLi
- 6) Grubbs^{2nd}, *then* MOMCl, *i*-Pr₂NEt, TBAI
- 7) O₃, *then* PPh₃, *then* piperidine, AcOH, *then* KOH
- 8) I₂, pyridine



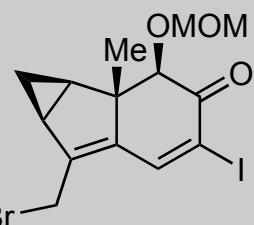
- 9) **2**, Cul, CsF, Pd(PPh₃)₄
- 10) DBU, 130 °C
- 11) TMSCl

- 1) Propose a mechanism
Hint for Step 1: β -lactone is formed
- 3) Hint: lactonization and elimination
- 4) Name? Corey–Chaykovsky
- 5) Hemiacetal is formed
- 6) Hemiacetal opens after RCM: why?
- 7) Two rings are formed after ozonolysis



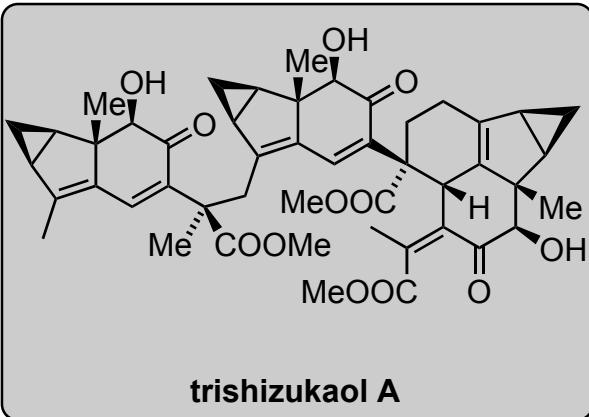
A

9'-11'

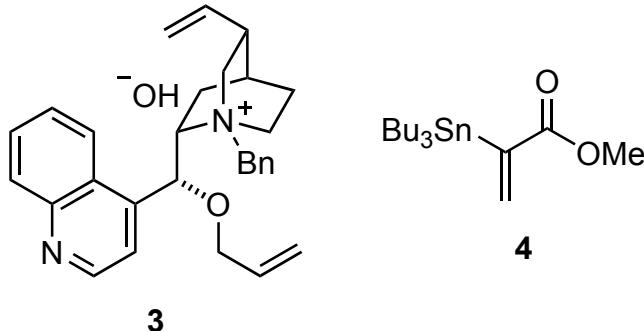


B + C

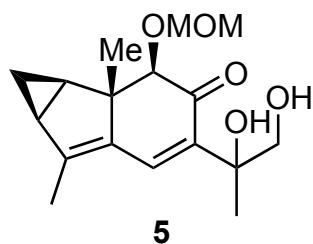
12-18



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



- 12) 3, CsOH , MnSO_4 , H_2O , toluene
13) NaClO_2 , NaH_2PO_4 , isopentene, *t*-BuOH
then TMSCHN_2
14) 4, CuI , CsF , $\text{Pd}(\text{PPh}_3)_4$
15) 5, PhCOOH , 170 °C
16) O_2 , methylene blue, $\text{h}\nu$, HCl , MeOH
17) KOH
18) TMSCHN_2 , MeOH



9') Name? Riley oxidation

11') Name? Appel reaction

12) What is the role of 3? chiral phase transfer catalyst

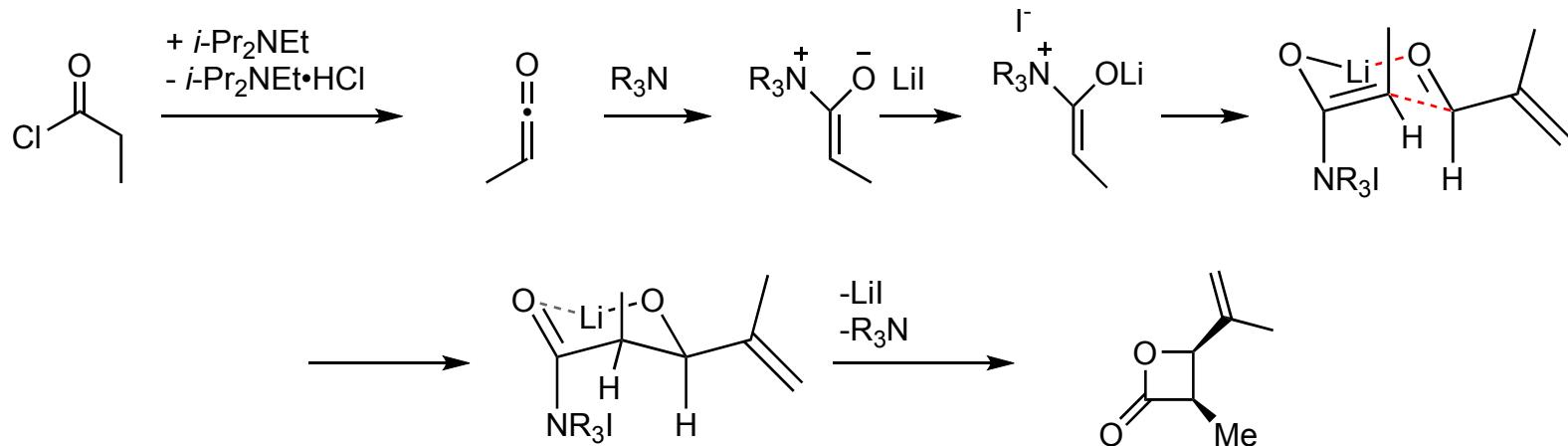
13) Name? Pinnick–Kraus oxidation

14) Name? Stille coupling

15) Hint: 5 first undergoes an intramolecular cyclization/elimination/isomerisation sequence to form a heterocycle before it participates in an intermolecular cyclization with the product of step 14

Key for 1):

J. Am. Chem. Soc. **2004**, *126*, 5352.



Key for 6): strain release of the *trans*-5/6 bicyclic