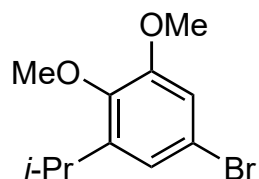
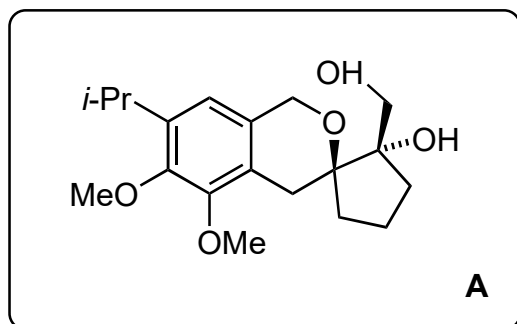


**Tandem C–H oxidation/cyclization/rearrangement and its application to asymmetric syntheses of
(–)-brussonol and (–)-przewalskine E**

Jiao Z.; Tu Y.; Zhang Q.; Liu W.; Zhang S.; Wang S.; Zhang F.; Jiang S.
E. Nat. Commun. **2015**, 7332, 6.

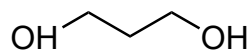


1-7

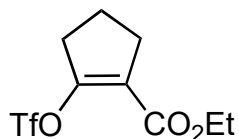


8-11

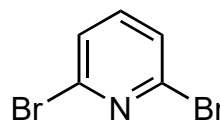
- 1) *n*-BuLi then DMF
- 2) **1**, CH(OEt)₃, (*n*-Bu)₄N⁺Br₃⁻
- 3) *n*-BuLi then CH₂O
- 4) PPh₃, CBr₄
- 5) Zn then **2**, Pd(Ph₃P)₂Cl₂ then aq. HCl
- 6) DIBAL-H
- 7) (–)-DET, Ti(*i*-PrO)₄, *t*-BuO₂H



1



2

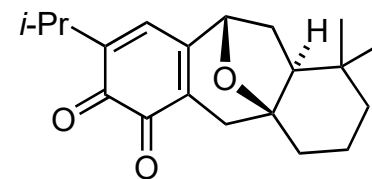


3

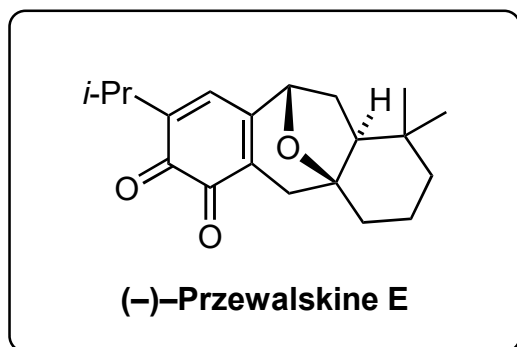
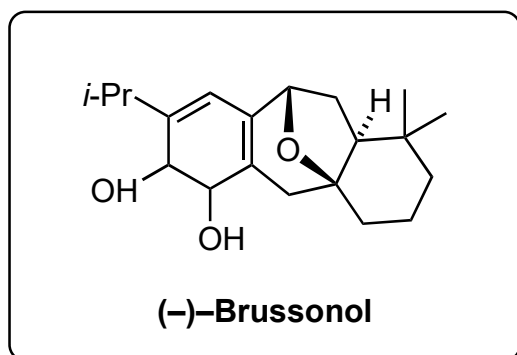
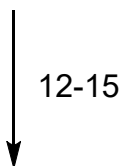
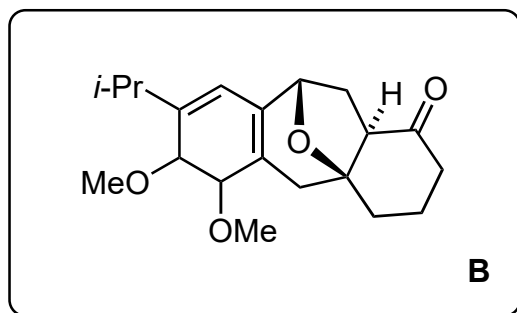
- 8) DMSO, DIPEA, SO₃•Py
- 9) Ph₃PCH₃Br, *t*-BuOK
- 10) TBSOTf, Et₃N
- 11) 4 Å MS, **3**, InCl₃, DDQ

7) Name the reaction and describe the mechanism. (hint: a spirocycle is formed)
Sharpless epoxidation (mechanism below)

11) Propose a mechanism. (note: two pathways are proposed by the authors)
(mechanisms below)



(–)-Przewalskine E



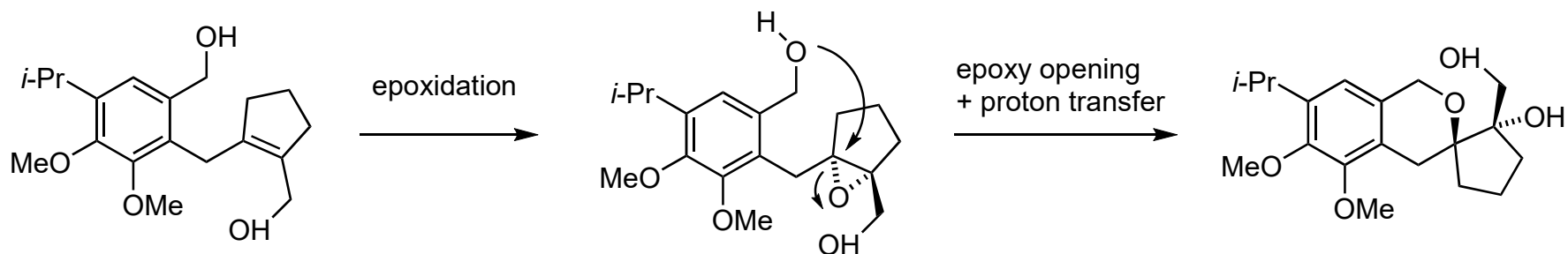
- 12) $\text{Ph}_3\text{PCH}_3\text{Br}$, *t*-BuOK
 13) Et_2Zn , CH_2I_2
 14) PtO_2 , H_2 , AcOH
 15) EtSH, NaH

13) Name the reaction.
Simmons-Smith cyclopropanation

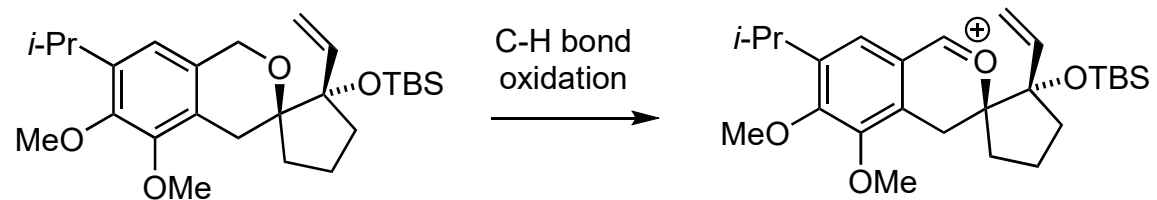
- 16) Ag_2O

16) Provide a name for the bridged bicyclic ring present in the molecule using IUPAC nomenclature.
oxabicyclo[3.2.1]octene

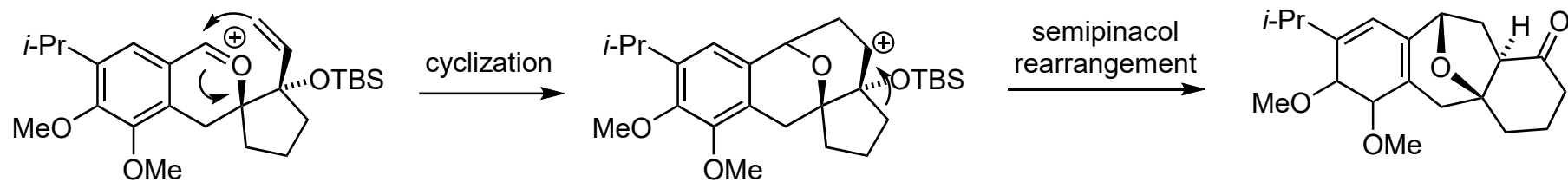
solution to step 7:



solution to step 11:



pathway a:



pathway b (likelier pathway as described by authors):

