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

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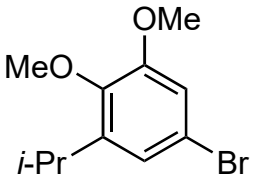


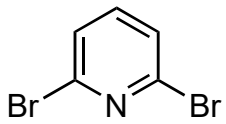
1-7

A

8-11

1) *n*-BuLi *then* DMF
2) **1**, $CH(OEt)_3$, $(n\text{-}Bu)_4N^+Br_3^-$
3) *n*-BuLi then CH_2O
4) PPh_3, CBr_4
5) Zn *then* **2**, $Pd(Ph_3P)_2Cl_2$ *then* aq. HCl
6) DIBAL-H
7) (**–**)-DET, $Ti(i\text{-}PrO)_4$, $t\text{-}BuO_2H$

1



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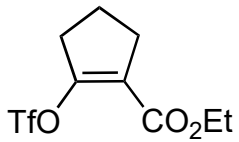
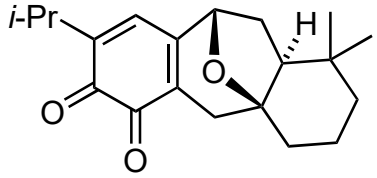


2

8) DMSO, DIPEA, SO_3•Py
9) Ph_3PCH_3Br, *t*-BuOK
10) TBSOTf, Et_3N
11) 4 Å MS, **3**, $InCl_3$, DDQ

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

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



(–)–Przewalskine E

B

12-15

12) Ph_3PCH_3Br, *t*-BuOK
13) Et_2Zn, CH_2I_2
14) PtO_2, H_2, AcOH
15) EtSH, NaH

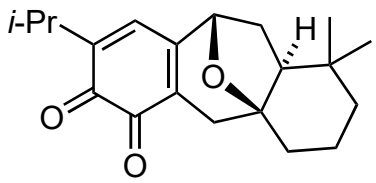
13) Name the reaction.

(–)–Brussonol

16

16) Ag_2O

16) Provide a name for the bridged bicyclic ring present in the molecule using IUPAC nomenclature.



(–)–Przewalskine E