Asymmetric Total Synthesis of Alstrostine G Utilizing a Catalytic Asymmetric Desymmetrization Strategy

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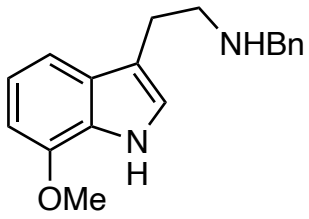
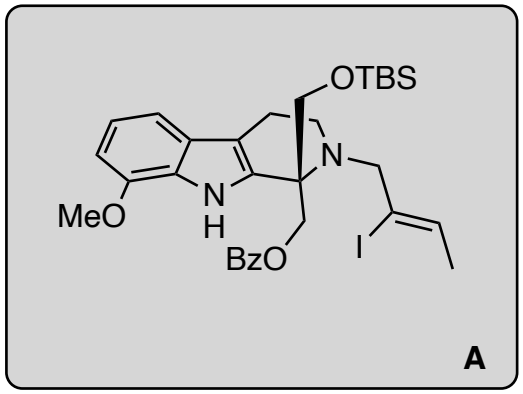
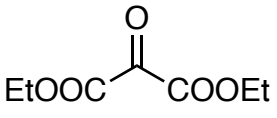


1–6



7–11

1) **1**, conc. HCl, EtOH, Δ
2) $LiAlH_4$ (2.5 equiv.)
3) **2**, $CuCl_2$, BzCl, NEt_3, –78 °C
4) TBSOTf, lutidine
5) Pd/C, H_2
6) **3**, K_2CO_3, 70 °C



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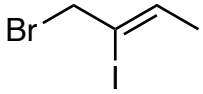

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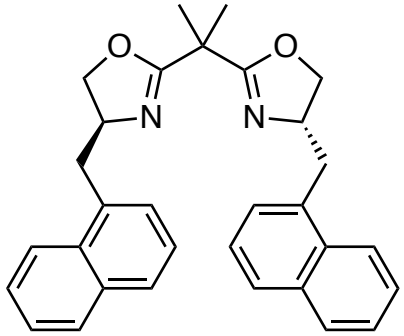
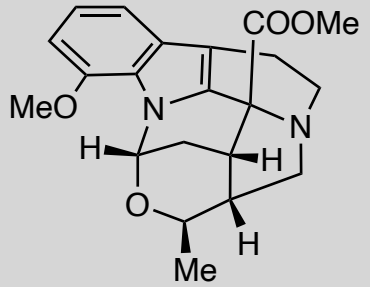


2

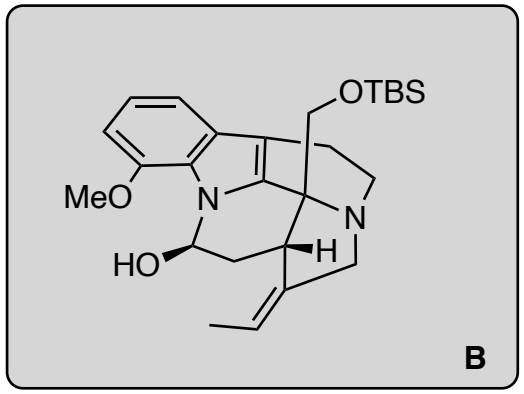
7) DIBAL-H (2.5 equiv.), 0 °C
8) DMP
9) NaH, $(EtO)_2P(O)CH_2COOEt$
10) DIBAL-H (3.0 equiv.), 0 °C
11) $Pd(OAc)_2$, PPh_3, NEt_3, 90 °C

1) Name of the reaction? *Pictet–Spengler.*
3) *Hint*: Read title.

9) Name of the reaction? *HWE.*
11) Hint: two rings are formed. Name of the reaction? Please draw the mechanism. *Heck cyclization.*

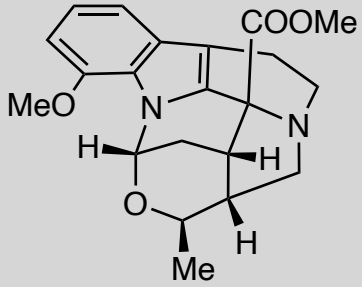


(+)-Alstrostine G



B

12–18

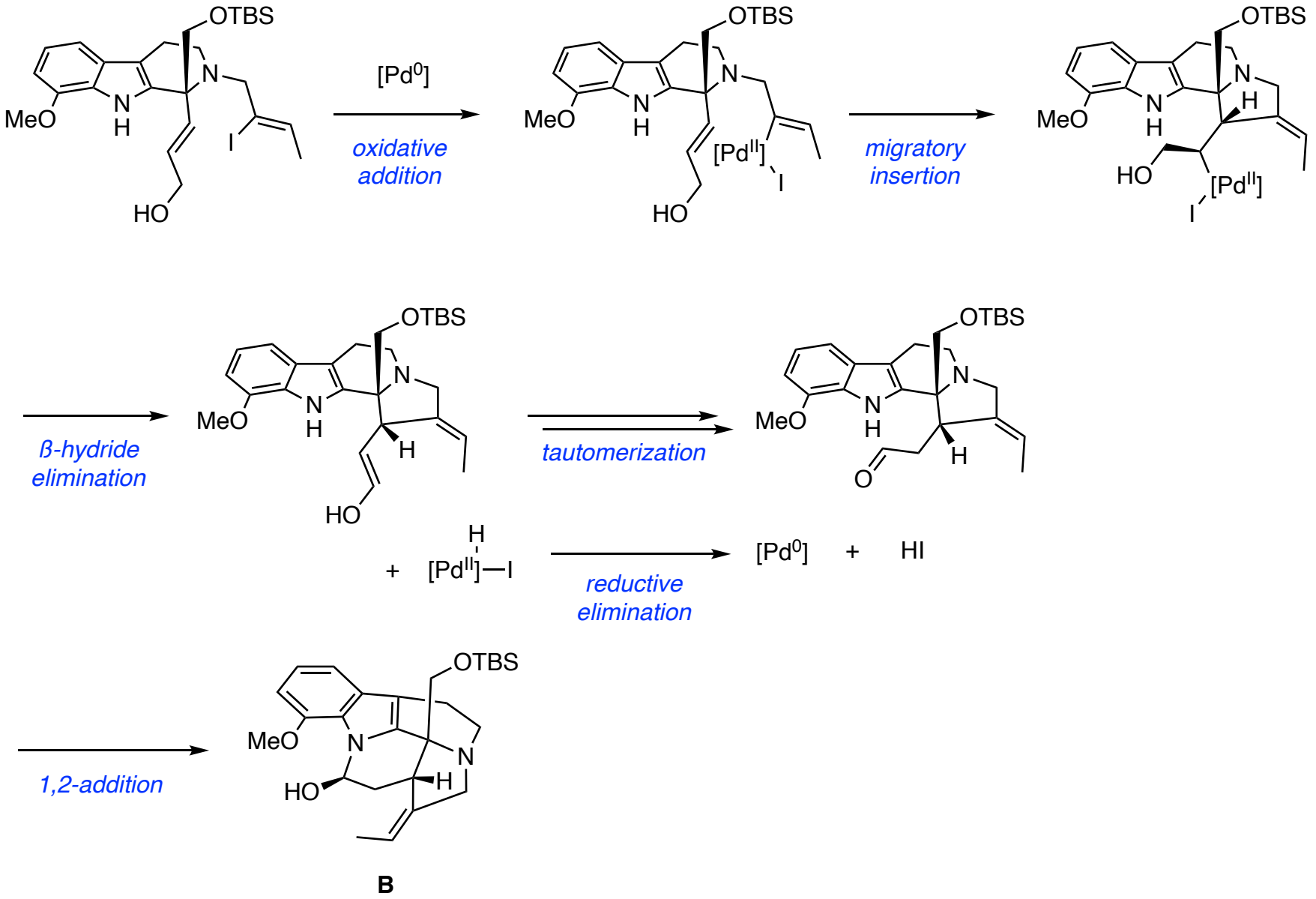


(+)-Alstrostine G

12) TMS-imidazole
13) $K_2OsO_4 \cdot 2H_2O$, citric acid, NMO, *t*-BuOH/H_2O
14) DMP
15) SmI_2 *then* $NaBH_4$
16) $BF_3 \cdot OEt_2$ *then* TBAF
17) IBX, 60 °C
18), I_2, KOH, MeOH

16) *Hint*: one ring is formed.

Mechanism for step 11)



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