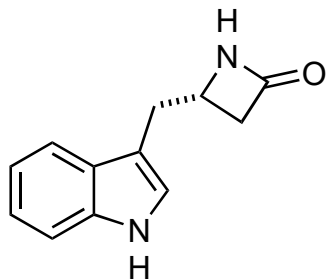
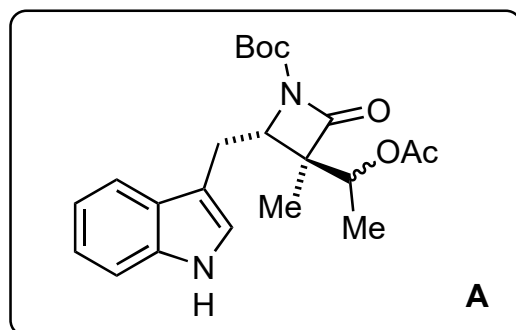


Total Synthesis of Indole Alkaloid (+)-Alstonlarsine A

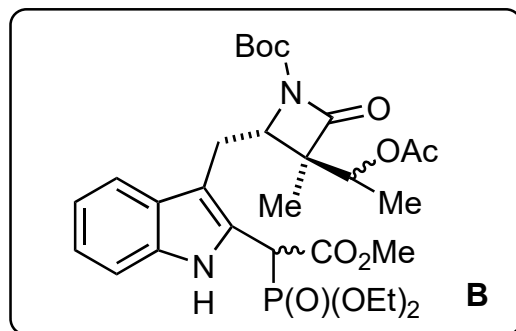
Z. Ferjancic, A. Kukuruzar, F. Bihelovic
Angew. Chem. Int. Ed. **2022**, 61, e202210297



1-8

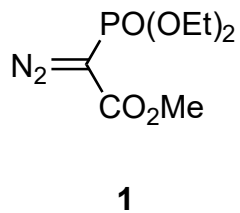


9



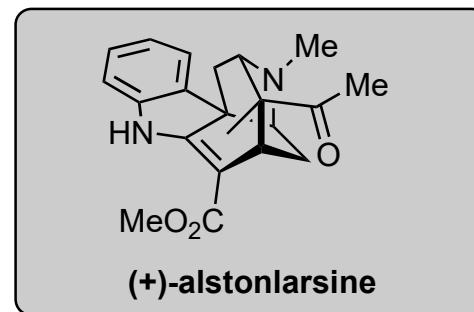
- 1) DMAP (10 mol%), TBSCl, Et₃N
- 2) NaH, TBSCl, 0 °C to r.t.
3. LDA, THF, –78 °C then MeI
- 4) Et₂NLi, THF, –78 °C
then MeCHO, –100 °C
- 5) DMAP, Ac₂O, Et₃N
- 6) KF, MeOH, 0 °C
- 7) DMAP (20 mol%), (Boc)₂O, Et₃N
- 8) 50% aq HF

- 9) Cu(acac)₂ (2 mol%), **1**, 120 °C



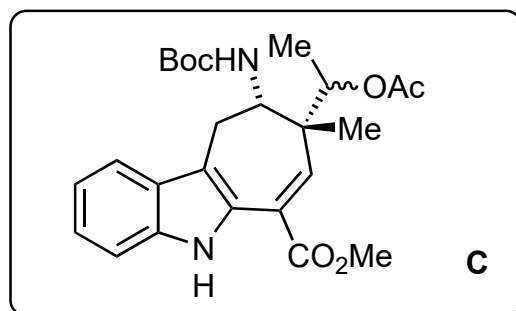
- 4) Name the reaction. *Aldol reaction.*

- 9) *Hint: a formal C-H insertion occurs.*

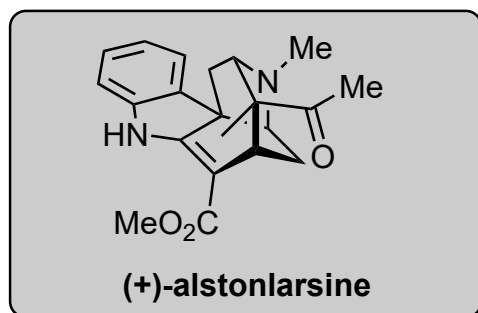


B

10-15



16-18

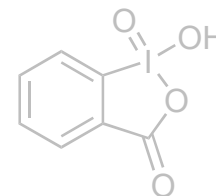


- 10) NaBH₄, MeOH/H₂O, 0 °C
- 11) PIDA, 75 °C
- 12) LiBr, Et₃N
- 13) (Boc)₂O, Et₃N, DMAP (10 mol%)
- 14) NaH, 0 °C
then MeI, 0 °C to r.t.
- 15) TFA

- 16) MeCHO, PhMe, 100 °C
- 17) NaH, LiAlH₄, THF, 0 °C
- 18) Me₂S, NCS, 0 °C
then **substrate**, -78 to -50 °C,
then Et₃N, -50 °C

11) Draw the structure of PIDA.

12) Name the reaction. Horner-Wadsworth-Emmons olefination.



phenyliodine(III) diacetate (PIDA)

16) Name the reaction. (inverse-electron-demand intramolecular dearomative) Diels-Alder cycloaddition.

18) Name the reaction. Corey-Kim oxidation.