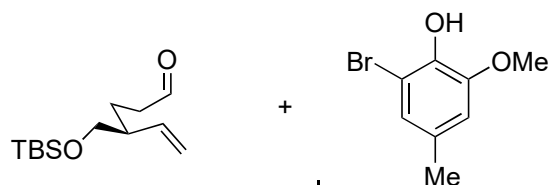


Total Synthesis of Vilmoraconitine

Ji, J.; Chen, J.; Qin, S.; Li, W.; Zhao, J.; Li, G.; Song, H.; Liu, X. Y.; Qin, Y. *J. Am. Chem. Soc.* **2023**, *145*, 3903–3908.



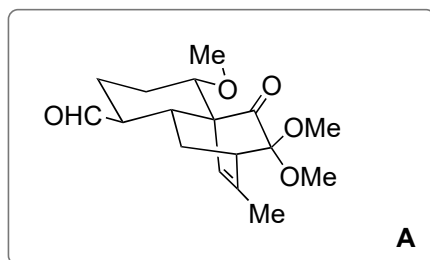
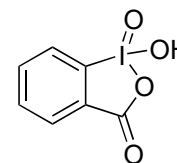
1-5

- 1) *n*-BuLi
- 2) Ph(OAc)₂, MeOH
- 3) 180 °C
- 4) NaH, MeI
- 5) TBAF *then* IBX

3) Name of the reaction?

IMDA

5) Structure of IBX?



A

6-11

- 6) MeI, *t*-BuOK
- 7) EtNH₂·HCl, NaBH₃CN
then NaOH, (Boc)₂O
- 8) LiAlH₄
- 9) *p*-TsOH
- 10) Sml₂
- 11) O₃, FeSO₄·7H₂O, MeOH,
4-methoxybenzenethiol

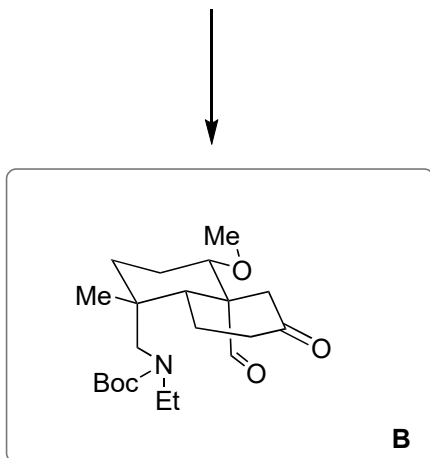
11) Who developed this protocol?

Prof. Kwon, UCLA

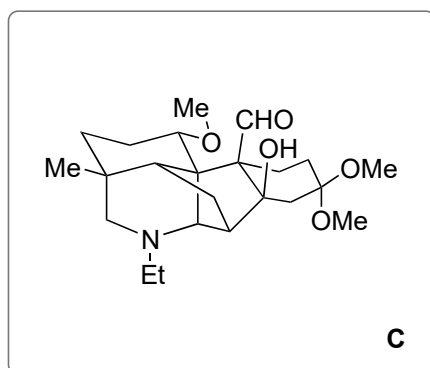
Hydrodealkynative fragmentation

Smaligo, A. J.; Swain, M.; Quintana, J. C.; Tan, M. F.; Kim, D. A.;

Kwon, O. *Science* **2019**, *364*, 681-685.



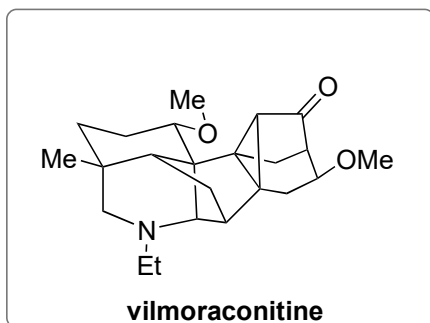
↓
12-18



- 12) TFA
- 13) LDA, Mander's reagent
- 14) Cs₂CO₃, MVK
- 15) KHMDS
- 16) TiCl₄, MeOH
- 17) LiAlH₄
- 18) AZADO, CuCl, bpy, DMAP, air

12) Name of the reaction?
hint Two new rings are formed
 Mannich reaction (cyclization)
18) Name of the reaction?
 Stahl oxidation

19-27



- 19) $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CN}$, LDA
- 20) TMSOTf
- 21) I_2 , NaHCO_3 , THF/ H_2O
- 22) TMP, TBSOTf
then 150 °C then p-TsOH
- 23) NaBH_4
- 24) MeI, *t*-BuOK
- 25) LDA, O_2 *then* SnCl_2 , aq. Na_2CO_3
- 26) LiAlH_4
- 27) AZADO, CuCl, bpy, DMAP