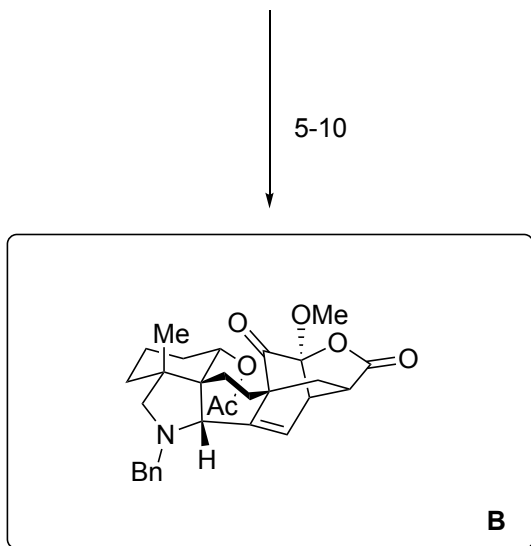
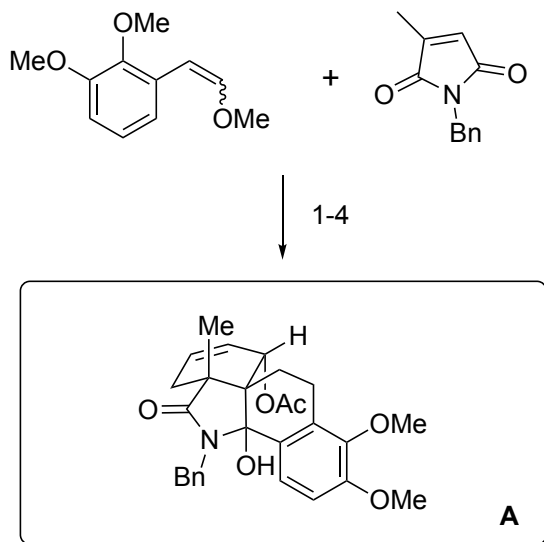
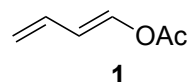


Total Synthesis of the Diterpenoid Alkaloid Arcutinidine Using a Strategy Inspired by Chemical Network Analysis

K. R. Owens, S. V. McCowen, K. A. Blackford, S. Ueno, Y. Hirooka, M. Weber, R. Sarpong
J. Am. Chem. Soc. **2019**, *141*, 13713–13717.

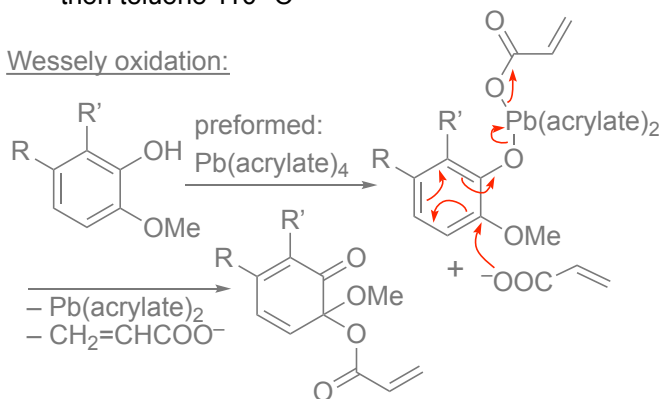


- 1) PPh₃, AcOH, 125 °C
- 2) DBU, THF
- 3) TfOH, CH₂Cl₂
- 4) **1**, AlCl₃, CH₃CN, 40 °C
single diastereomer!



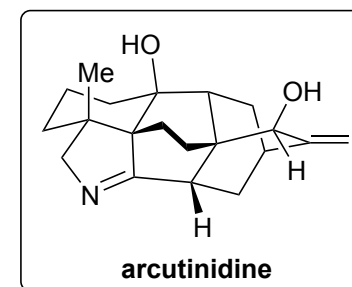
- 5) Rh/Al₂O₃, EtOAc, H₂
- 6) BF₃·OEt₂, Et₃SiH
- 7) LiAlH₄
- 8) Ac₂O, DMAP, pyridine
- 9) TMSI
- 10) acrylic acid (60 equiv.), Pb(OAc)₄, 0 °C
 then toluene 110 °C

Wessely oxidation:

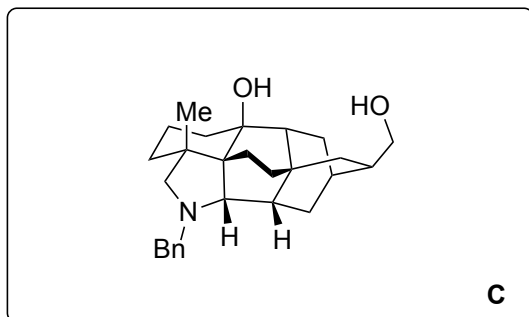


1): is a modified version of what named reaction? Wittig reaction
hint: in 2) an isomerization is performed
 3) and 4): name the reactions
 Friedel-Crafts cyclization and Diels-Alder cycloaddition

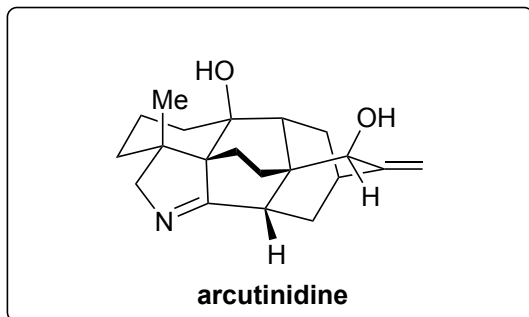
hint: in 9) reaction occurs once per molecule
 10): name reactions and propose a mechanism for the first reaction
 Wessely oxidation (mech. below),
 Diels-Alder



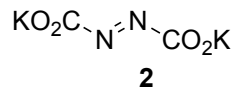
11-18



19-23



- 11) MeOH, then $\text{SmI}_2/\text{H}_2\text{O}$, 23 °C
- 12) Amberlyst® 15, MeOH, 100 °C microwave
- 13) DMP, NaHCO_3 , H_2O
- 14) SmI_2 , 23 °C
- 15) **2**, AcOH, MeOH, 50 °C
- 16) InCl_3 , Ph_2SiH_3
- 17) LiAlH_4
- 18) $\text{Mn}(\text{dpm})_3$, PhSiH_3 , EtOH, O_2

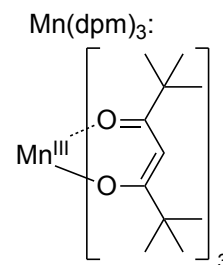


- 19) $\text{Pd}(\text{OH})_2/\text{C}$, H_2
- 20) NCS, DBU
- 21) MsCl, Et_3N , 23 °C
- 22) DBU, NaI, 80 °C
- 23) SeO_2

note: Amberlyst® 15 is a polystyrene based ion exchange resin with sulfonic groups
14): name reaction pinacol coupling

hint: in 16) an elimination is followed by a deoxygenation

18): name reaction Mukaiyama hydration



23): name reaction Riley oxidation