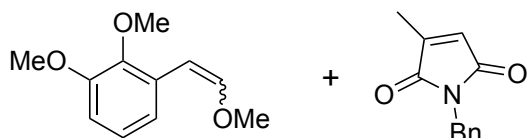


Total Synthesis of the Diterpenoid Alkaloid Arcutinidine Using a Strategy Inspired by Chemical Network Analysis

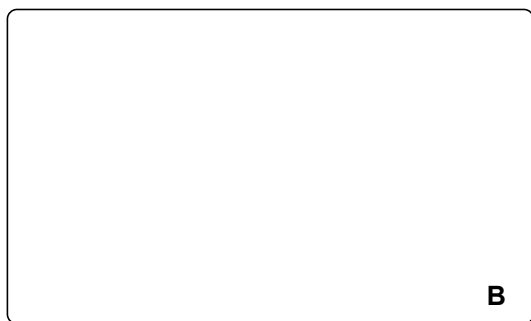
K. R. Owens, S. V. McCowen, K. A. Blackford, S. Ueno, Y. Hirooka, M. Weber, R. Sarpong
J. Am. Chem. Soc. **2019**, *141*, 13713–13717.



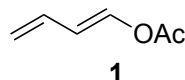
1-4



5-10



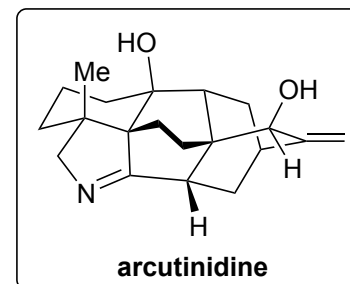
- 1) PPh_3 , AcOH, 125 °C
- 2) DBU, THF
- 3) TfOH, CH_2Cl_2
- 4) **1**, AlCl_3 , CH_3CN , 40 °C
single diastereomer!



- 5) $\text{Rh}/\text{Al}_2\text{O}_3$, EtOAc, H_2
- 6) $\text{BF}_3 \cdot \text{OEt}_2$, Et_3SiH
- 7) LiAlH_4
- 8) Ac_2O , DMAP, pyridine
- 9) TMSI
- 10) acrylic acid (60 equiv.), $\text{Pb}(\text{OAc})_4$, 0 °C then toluene 110 °C

1): is a modified version of what named reaction?
hint: in 2) an isomerization is performed
3) and 4): name reactions

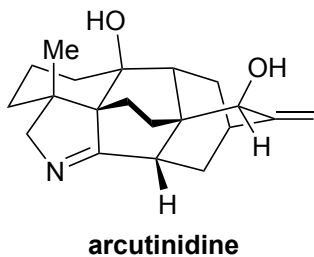
hint: in 9) reaction occurs once per molecule
10): name reactions and propose a mechanism for the first reaction



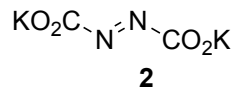
11-18



19-23



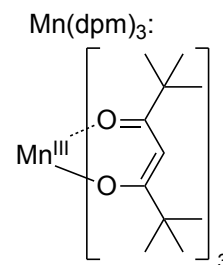
- 11) MeOH, then SmI_2 (up to 10 equiv), H_2O , 23 °C
- 12) Amberlyst® 15, MeOH, 100 °C microwave
- 13) DMP, NaHCO_3 , H_2O
- 14) SmI_2 , 23 °C
- 15) **2**, AcOH, MeOH, 50 °C
- 16) InCl_3 , Ph_2SiHCl
- 17) LiAlH_4
- 18) $\text{Mn}(\text{dpm})_3$, PhSiH_3 , EtOH, O_2



- 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

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



23): name reaction