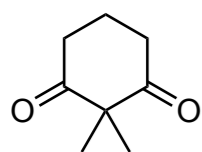
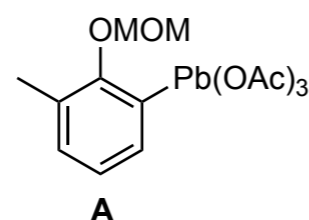


Total Synthesis of (±)-Maoecrystal V

J. Gong, G. Lin, W. Sun, C.-C. Li, Z. Yang, *JACS* **2010**, 132, 16745–16745.



- 1) TsNHNH₂, EtOH
- 2) ethylene glycol, OHCH₂CH₂ONa, 180 °C
- 3) Me₂CO₃, NaH, THF, Δ
- 4) **A**, pyr, CHCl₃
- 5) (*n*-Bu₄)NBH₄, MeOH
- 6) LAH, THF



Step 2: Name Reaction and Mechanism? Bamford-Stevens Reaction (in protic solvent)
-> via carbo cation (vs. via carbene)

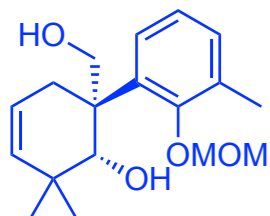
Step 4: Name Reaction? Pinhey Arylation

Step 5+6: Please come up with a rationale for a 2-step strategy instead of a one-pot reduction.

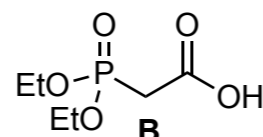
DIBAL and LAH gave wrong diastereomer (1:6)

-> also organoboranes, NaBH₄/Lewis Acid and hydrosilanes gave wrong diastereomer

-> ammonium borhydride: desired selectivity due to directing and accelerating effect of the cationic-π-interaction between ammonium salt and the phenyl ring of the substrate, which delivers the hydride to the ketone from its top face



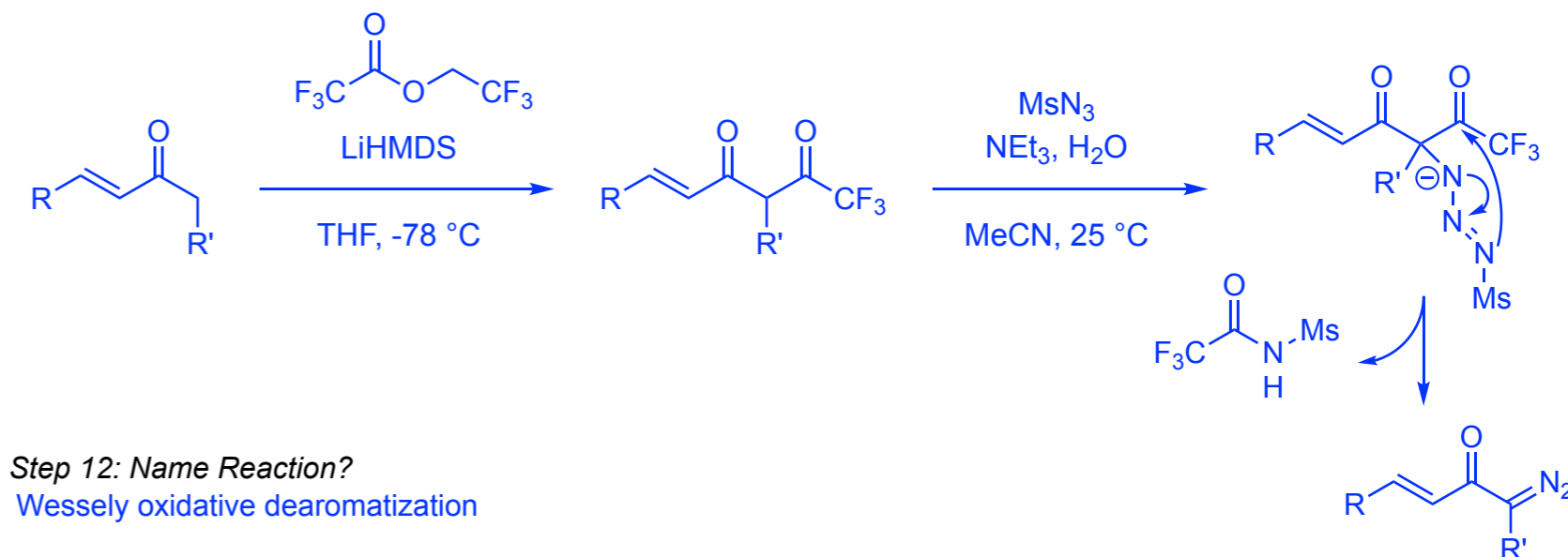
- 7) **B**, EDCI, DMAP, CH₂Cl₂
- 8) DBU, TsN₃, CH₂Cl₂
- 9) Rh₂(OAc)₄, benzene, reflux
- 10) (HCHO)_n, *t*-BuOK, THF



Step 8: Name Reaction? Usually this reaction works only for 1,3-dicarbonyl compounds. Do you know a 2-step procedure to transform simple ketones into the desired product?

Regitz Diazotransfer

(Danheiser Modification using hexafluoro ethyl acetate)



Step 12: Name Reaction?

Wessely oxidative dearomatization

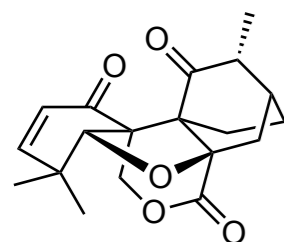
Step 18: composition of Lindlar cat.?

Pd-CaCO₃

Pb(OAc)₂

quinoline

- 11) TFA, CH₂Cl₂
- 12) Pb(OAc)₄, AcOH, 0 °C
- 13) PhMe, 145 °C
- 14) NBS, benzoyl peroxide, CCl₄, reflux
- 15) Bu₃SnH, TEMPO, PhH, reflux
- 16) Zn, AcOH, THF/H₂O
- 17) Sml₂, THF, MeOH
- 18) Lindlar cat.
- 19) DMP
- 20) DBU, PhMe, 100 °C



Maoecrystal V