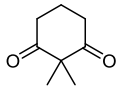
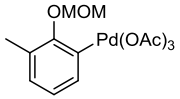
Total Synthesis of (±)-Maoecrystal V

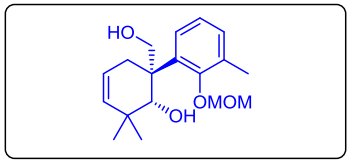
J. Gong, G. Lin, W. Sun, C.-C. Li, Z. Yang, *JACS* **2010**, 132, 16745–16745.



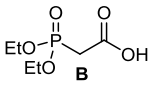
1) $TsNHNH_2$, EtOH
2) ethylene glycol, $OHCH_2CH_2ONa$, 180 °C
3) Me_2CO_3, NaH, THF, Δ
4) **A**, pyr, $CHCl_3$
5) $(n\text{-}Bu_4)NBH_4$, MeOH
6) LAH, THF



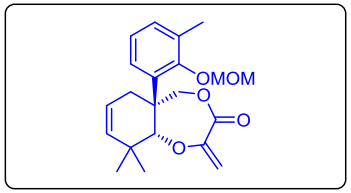
A



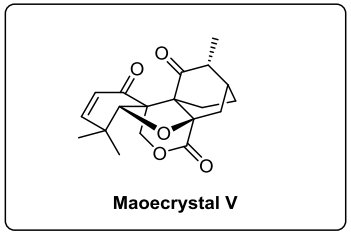
7) **B**, EDCI, DMAP, CH_2Cl_2
8) DBU, TsN_3, CH_2Cl_2
9) $Rh_2(OAc)_4$, benzene, reflux
10) $(HCHO)_n$, *t*-BuOK, THF



B



11) TFA, CH_2Cl_2
12) $Pb(OAc)_4$, AcOH, 0 °C
13) PhMe, 145 °C
14) NBS, benzoyl peroxide, CCl_4, reflux
15) Bu_3SnH, TEMPO, PhH, reflux
16) Zn, AcOH, THF/H_2O
17) SmI_2, THF, MeOH
18) Lindlar cat.
19) DMP
20) DBU, PhMe, 100 °C



Maoecrystal V

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

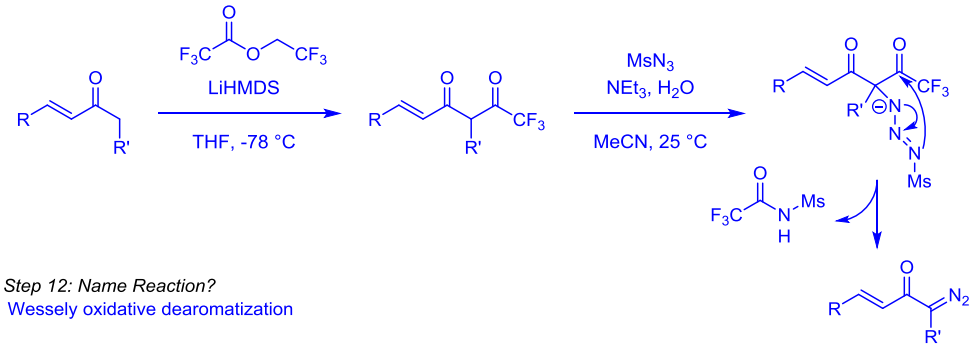
Step 4: Name Reaction? Pinhey Arylation

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, $NaBH_4$/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

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.?
$Pd\text{-}CaCO_3$
$Pb(OAc)_2$
quinoline