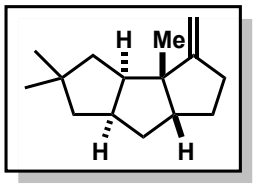
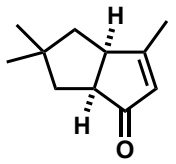
Selected Syntheses (5 / >25) of Hirsutene



$C_{15}H_{24}$



C_2H_4, *hv*, 75% → $Ph_3P{=}CH_2$, 92% → $Tl(ClO_4)_3$, *t*-BuOH-H_2O, r.t. 24h, 57%

hint 1

A

$C_{14}H_{22}O$

$NaBH_4$, 100% → **1*eq.*** PTSA, PhH, 80°C 2h, 70% → LAH, 97% → $CrO_3{\cdot}H_2SO_4$ 95%

hint 2

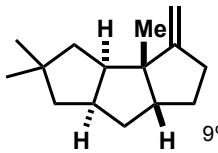
B

$C_{14}H_{22}O$

$Ph_3P{=}CH_2$, 92% → ***cat.*** PTSA, PhH, 80°C 20min, 95%

C

m-CPBA, 98% → LAH → MsCl, pyr, 70%(o2s)

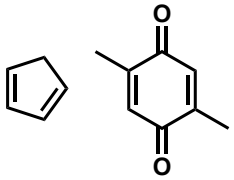


9%

+

C

61%



PhH, reflux, 90% → **E** $C_{13}H_{14}O_2$ → *hv*, EtOAc, 85% → **F** $C_{13}H_{14}O_2$ → 1mm Hg, 500°C "sublimation" *quant.*

hint 3

G

$C_{13}H_{14}O_2$

BnOBz (bp 324°C), reflux, 43% brsm

hint 4

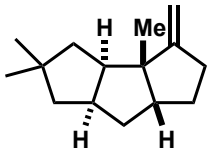
H

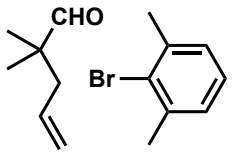
$C_{13}H_{14}O_2$

$Ph_3P{=}CH_2$, PhMe, 84% ← NaH, MeI, 65% ← H_2, Pd/C, 95%

I

n-Bu_3SnH, 19% ← NaH, CS_2 MeI, 88% ← LAH, 90%





Mg, then Ac_2O, 79% → *hv* → LAH, 22% (o2s)

J

4 rings

$C_{15}H_{22}O$

CSA, 71%

K

3 rings

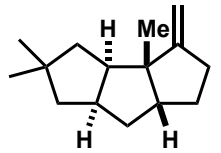
$C_{15}H_{20}$

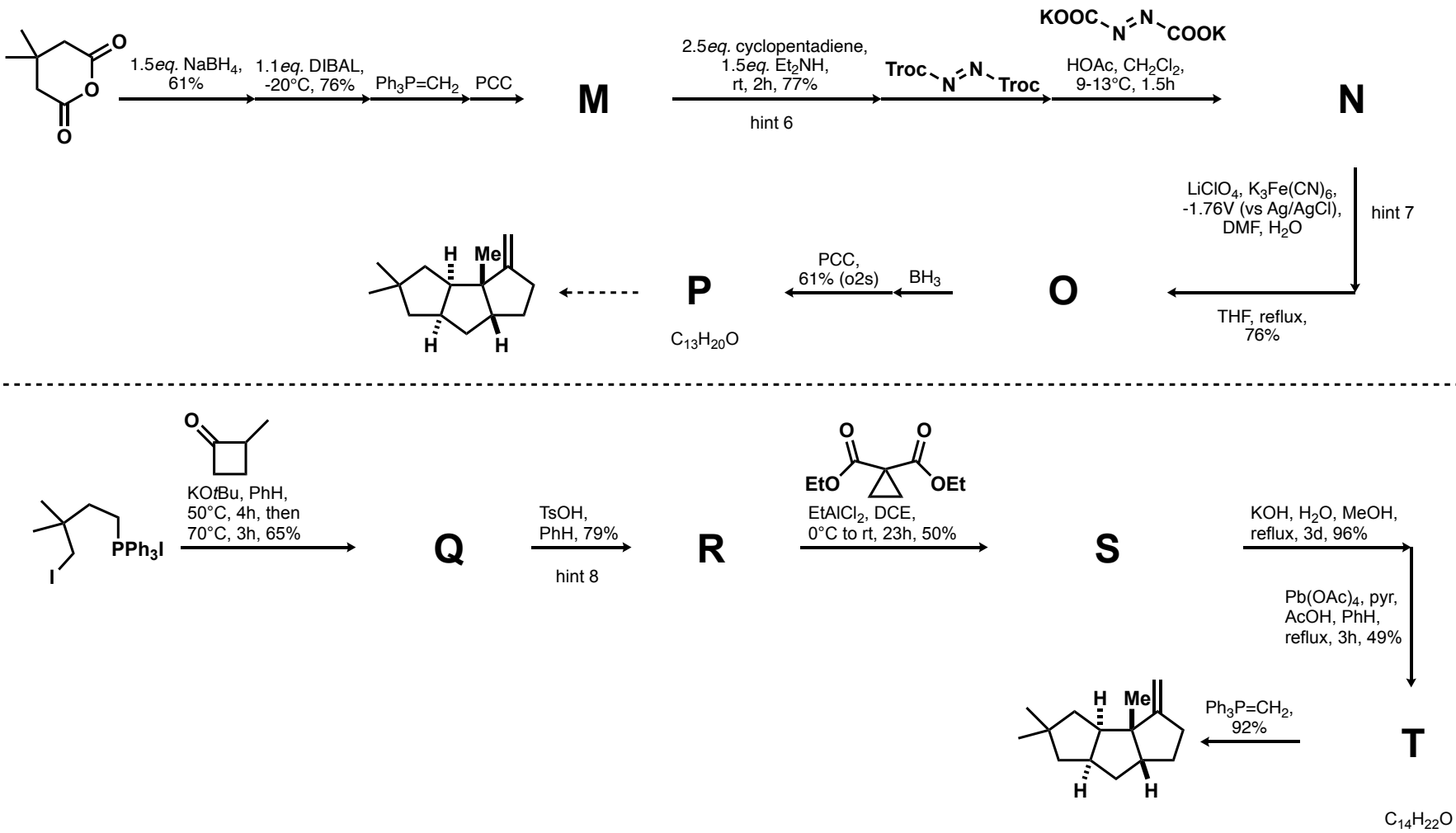
PhSH, neat 78%

hint 5

L

Crabtree, H_2 → $NaIO_4$, 86% → $P(OMe)_3$, 60%





hint 1 : Thallium Perchlorite has been effectively used for ring-expansions (in an oxidative fashion, Tl(I) generated), the 5 membered-side transfered in this case.
hint 2 : Rearrangement didn't work in a desired way.
hint 3 : Sublimation of **F** through a Pyrex Vigreux column heated to 500 "C at 1mmHg and direct crystallisation of the pyrolysate gave **G**. 3 rings in **G**
hint 4 : By comparing **G** (stereocenters!) with Hirsutene one should know the purpose of this step. This reaction went through a transposed bis-enone as an intermediate
hint 5 : "Radical conjugated addition"
hint 6 : not DA
hint 7 : Imagine what's needed in the following step, product of this step has the formular of $C_{13}H_{20}N_2$
hint 8 : **R** contains a tri-substituted olefin