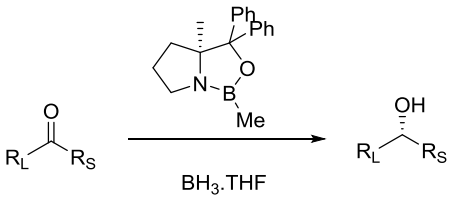
Problem Session Zsofi April 2014

Named Reactions:

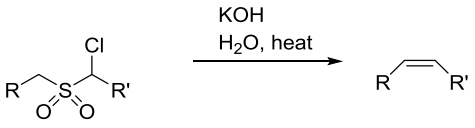
Give reaction name and/or mechanism.

1.



a) What is the origin of enantioselectivity? Draw a diagram.

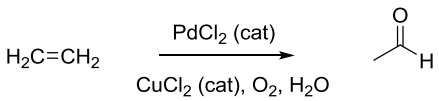
2.



a) What needs to be changed to yield the E-isomer?
b) Give the name and mechanism for a modification which includes *in situ* halogenation.

3.

4.

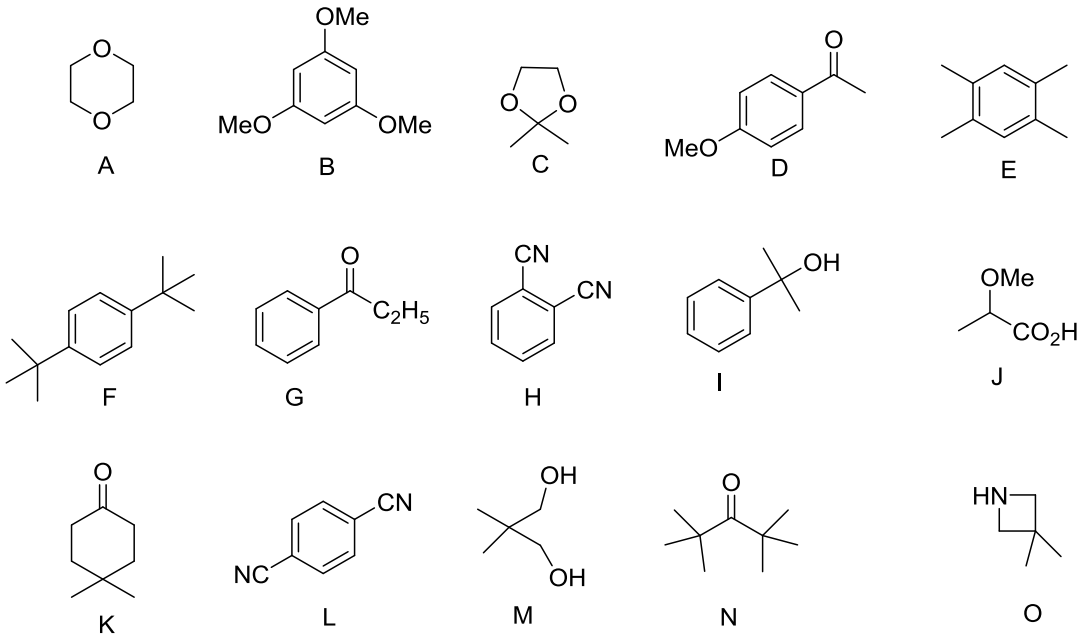


a) What is the name of the lab-scale modification to form ketones, and what are the reagents/catalysts?

NMR Problems:

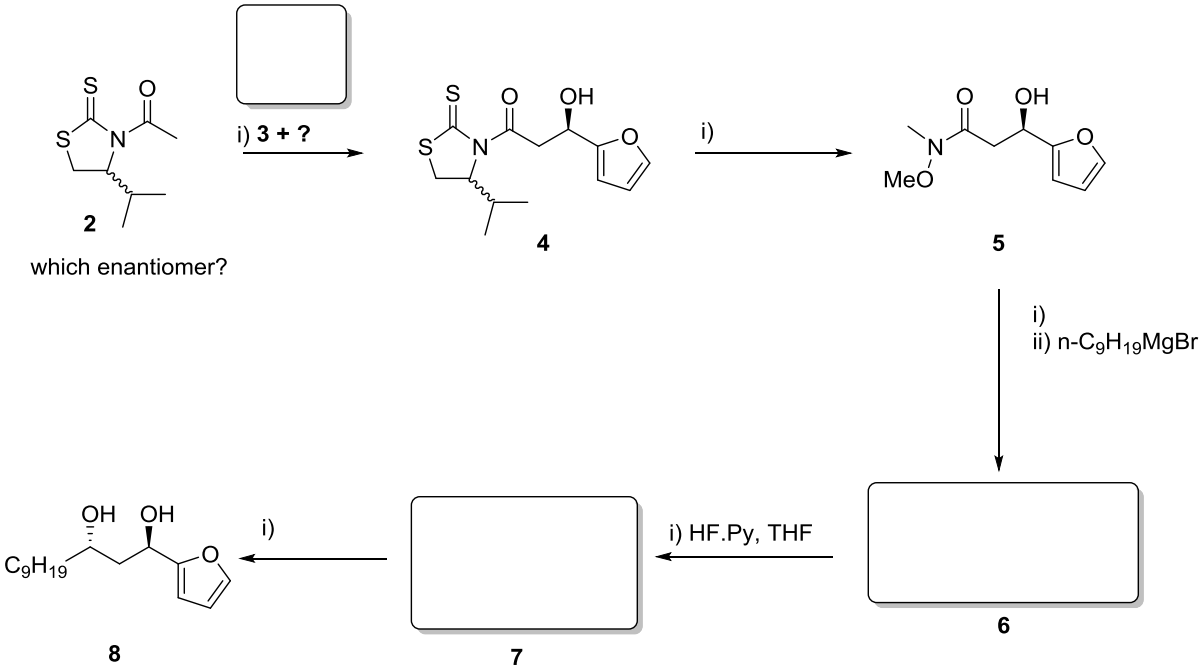
Eight structure elucidation problems based on ^{1}H nmr, ^{13}C nmr and some infrared spectroscopic data are presented below. In each case, from the 15 formulas shown at the bottom of the page (**A** through **O**), select that one which best fits the evidence.

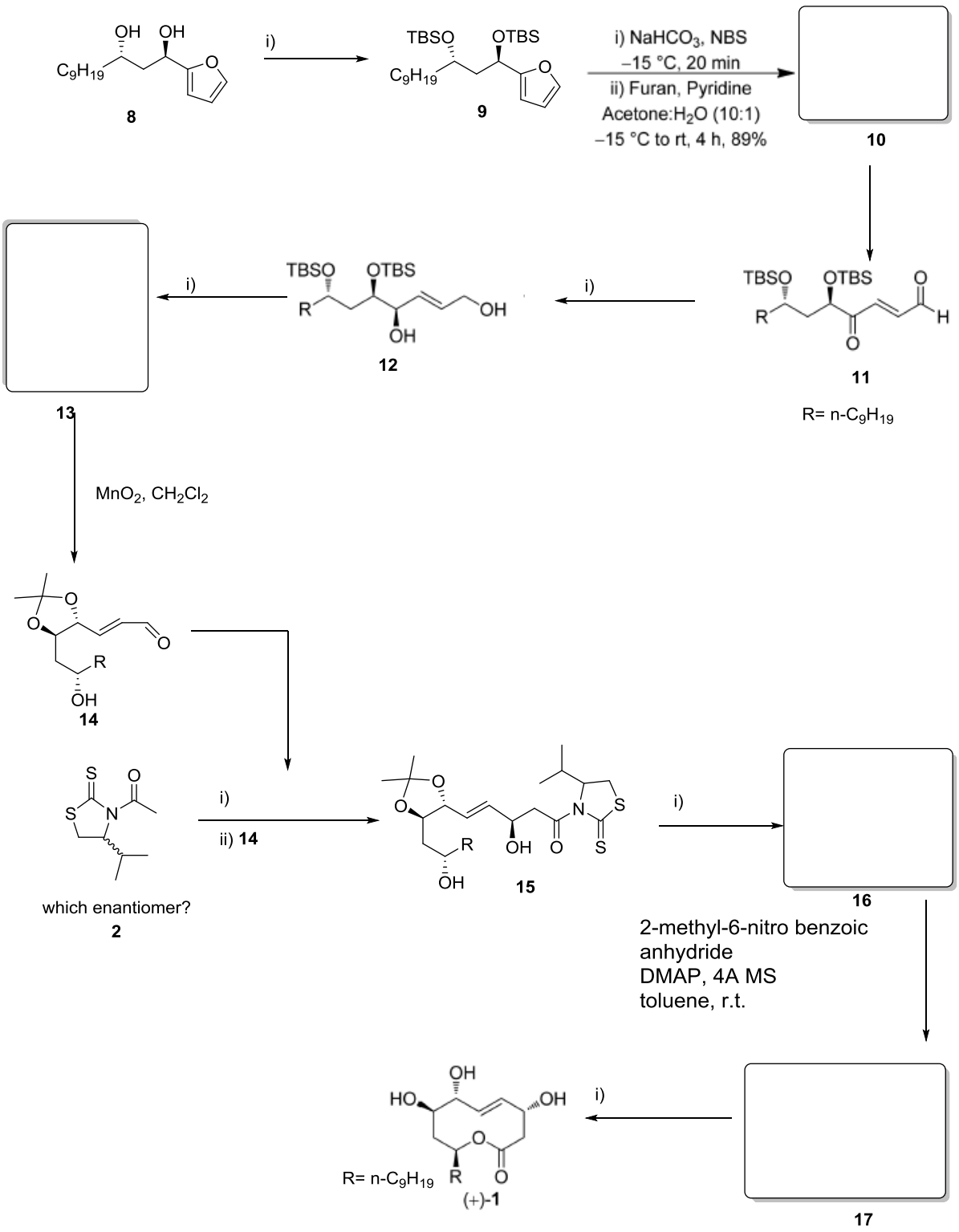
1. A $C_5H_{12}O_2$ compound has strong infrared absorption at 3300 to 3400 cm^{-1} The ^{1}H NMR spectrum has three singlets at δ 0.9 , δ 3.45 and δ3.2 ppm; relative areas 3:2:1. The ^{13}C NMR spectrum shows three signals all at higher field than δ100 ppm. Suggest a structure for this compound.
2. A $C_4H_8O_2$ compound has a strong infrared absorption at 1150 cm^{-1}, but no absorption at 3300 to 3400 cm^{-1}. It's ^{1}H NMR spectrum shows a singlet at δ 3.55 ppm. The ^{13}C NMR spectrum shows one signal at δ 66.5 ppm. Suggest a structure for this compound.
3. A $C_9H_{12}O$ compound has strong infrared absorption at 3300 to 3400 cm^{-1}. The ^{13}C NMR spectrum of this compound has six discrete signals. It's ^{1}H NMR spectrum has three sets of lines: singlets at δ1.1 (6H), 1.9 (1H) and 7.3 (5H) ppm. Suggest a structure for this compound.
4. A $C_{10}H_{14}$ compound. The ^{1}H NMR spectrum has two singlets at δ 2.45 and 7.0 ppm (ratio = 6:1). The ^{13}C NMR spectrum shows three signals at δ132.9, 130.5 and 18.9 ppm. Suggest a structure for this compound.
5. A $C_8H_4N_2$ compound shows a sharp infrared absorption at 2230 cm^{-1}. It's ^{1}H NMR spectrum has a singlet at δ 7.6 ppm. The ^{13}C NMR spectrum shows three signals at δ132, 119 and 117 ppm. Suggest a structure for this compound.
6. A $C_{14}H_{22}$ compound. The ^{1} H NMR spectrum has two singlets at δ 1.1 and 7.25 ppm (ratio = 9:2). The ^{13}C NMR spectrum shows four signals at δ 147, 125, 39.3 and 30.8 ppm. Suggest a structure for this compound.
7. A $C_9H_{12}O_3$ compound has strong infrared absorption near 1100 cm^{-1}. Its ^{1}H NMR spectrum has sharp singlet peaks at δ 3.6 and 6.6 ppm (intensity ratio 3:1). Its ^{13}C NMR spectrum shows three lines at δ 165, 115 and 55 ppm. Suggest a structure for this compound.
8. A $C_9H_{18}O$ compound has a strong infrared absorption at 1710 cm^{-1}. Its ^{1}H NMR spectrum has a single sharp peak (a singlet) at δ 1.2 ppm. Its ^{13}C NMR spectrum shows three lines at δ210, 45 and 25 ppm. Suggest a structure for this compound.



Total Synthesis

(+)-Seimatopolide A is a 10-membered lactone isolated from the fungus Seimatosporium discosioides. Seimatopolides are shown to activate the γ-subtype peroxisome prolifirator-activated receptors (PPAR-γ), which is an apparent pivotal process in the regulation of type 2 diabetes. Give the mechanism, and reagents or structure where appropriate for all steps.




OH
OH
C_9H_{19}
O
8
i)
TBSO
OTBS
C_9H_{19}
O
9
i) $NaHCO_3$, NBS
−15 °C, 20 min
ii) Furan, Pyridine
Acetone:H_2O (10:1)
−15 °C to rt, 4 h, 89%
10
TBSO
OTBS
R
O
H
O
11
R= n-C_9H_{19}
i)
TBSO
OTBS
R
OH
OH
12
i)
13
MnO_2, CH_2Cl_2
O
O
R
OH
O
14
S
O
S
N
which enantiomer?
2
i)
ii) 14
O
O
R
OH
OH
N
S
O
S
15
i)
16
2-methyl-6-nitro benzoic
anhydride
DMAP, 4A MS
toluene, r.t.
OH
HO
OH
O
R
O
R= n-C_9H_{19}
(+)-1
i)
17