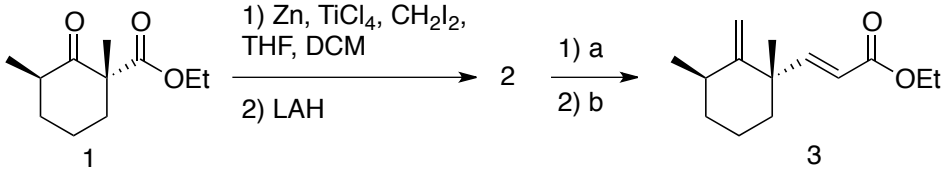
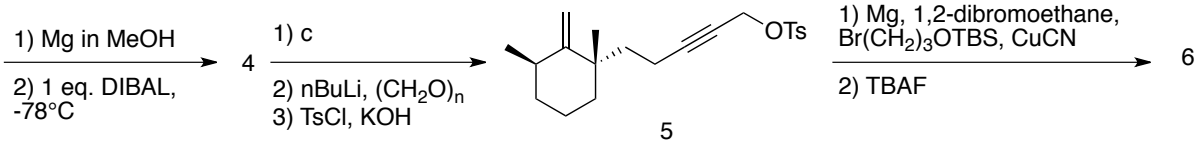
Exercise meeting, 28.06.2016
Submitted by Lars

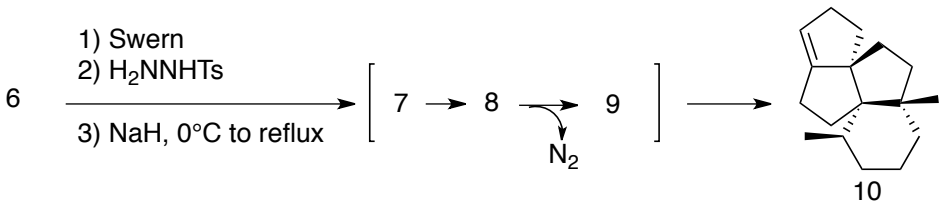
Waihoensene – A natural product without heteroatoms



Q1: convert **2** into **3** using two named reactions and give their mechanisms.

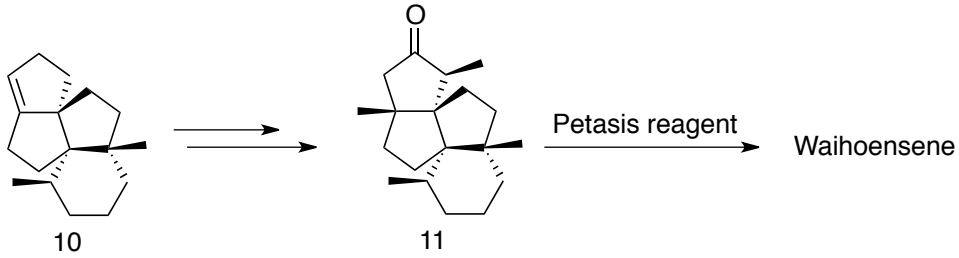


Q2: Give the structure of **4**.
Q3: What is the name and mechanism of transformation **c)**?
Q4: Give the structure of **6**.

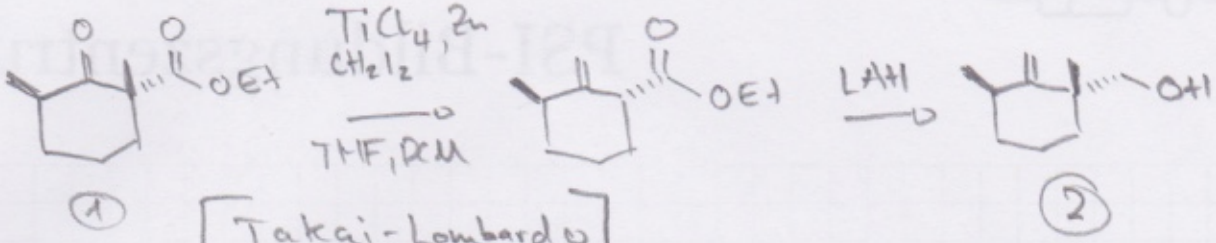


Q5: The key step of the synthesis was performed after Swern oxidation and p-toluenesulfonyl hydrazide treatment of **6**. Upon heating of the sodium salt of the hydrazone, the generated compound **7** is reacting spontaneously to the intermediate **8**. After loss of nitrogen, **10** was formed as the major compound from intermediate **9**. Give the structure of the intermediates **7**, **8** and **9**.

Q6: Explain the formation of **10** from **9**. Formation of **10** is favoured but by NMR, at least one other isomer was observed (but not isolated). Propose the structure of an isomer.



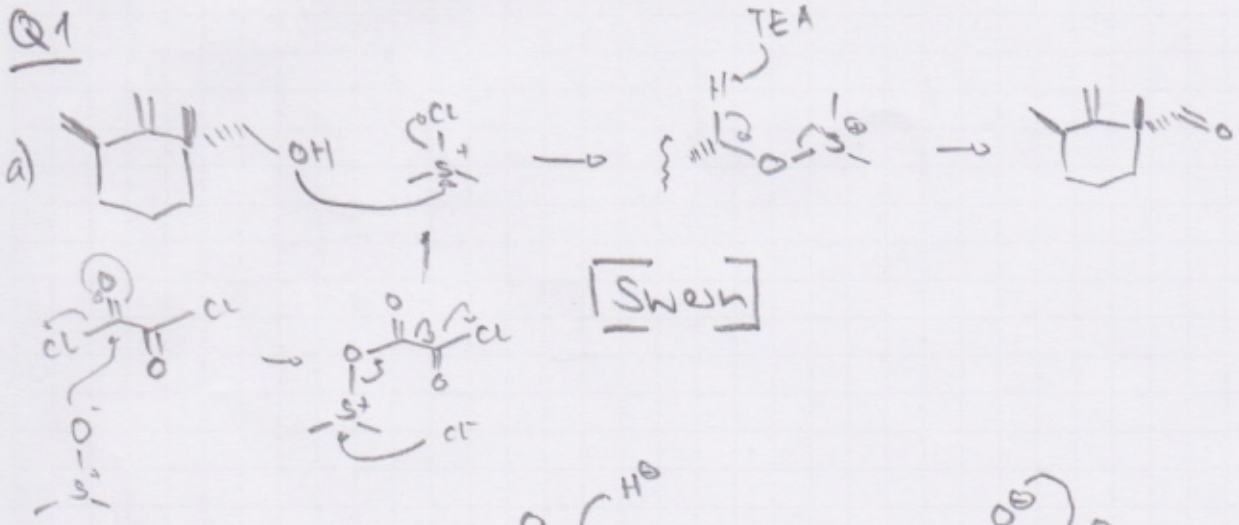
Q7: Give the structure of Waihoensene. Why could they not use the Petasis-reagent to convert **1** into **2**?



(1) (2)

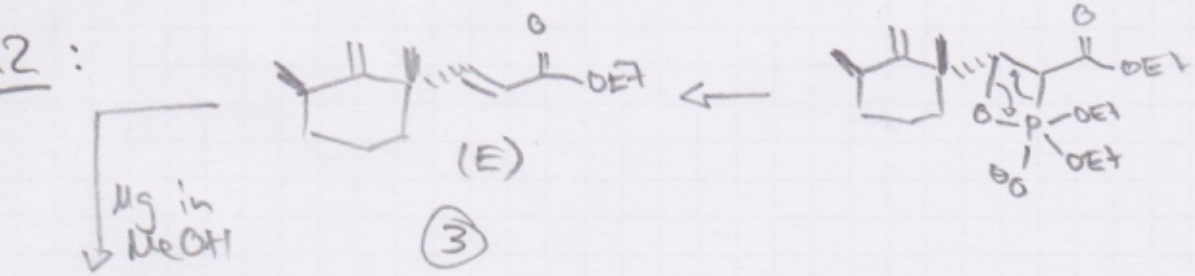
[Takai-Lombardo reaction]
(methenylation of sterically hindered ketones)

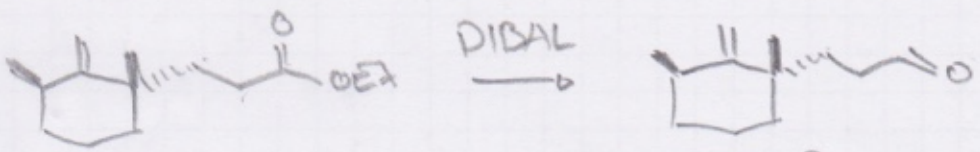
Q1



[Horner Wadsworth Emmons]

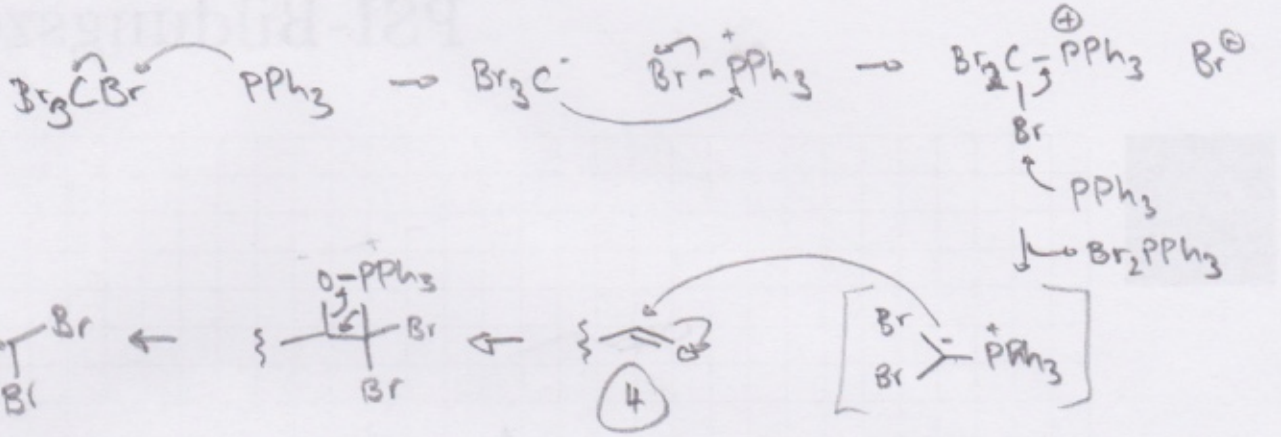
Q2:



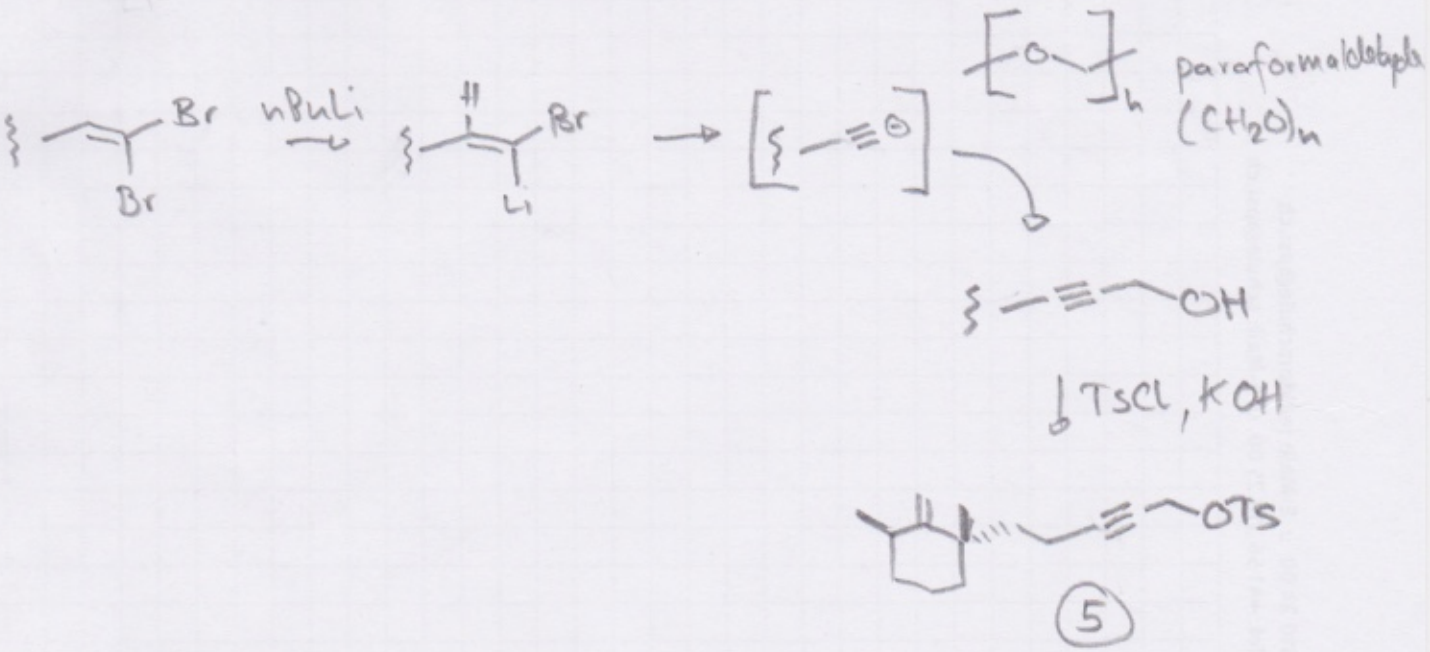


(4)

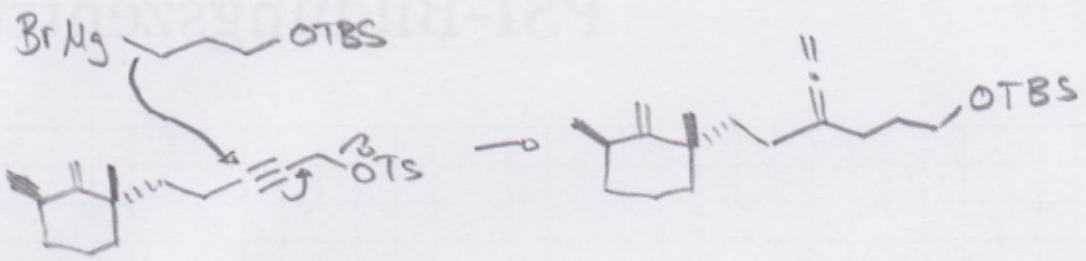
Q3

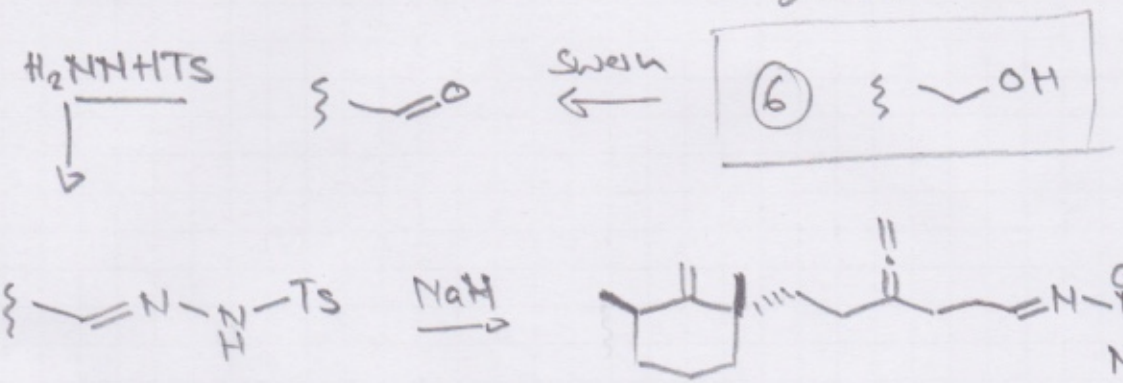


[Corey-Fuchs]

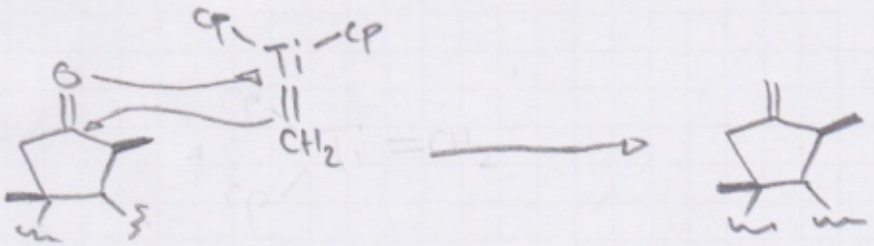


Q4:

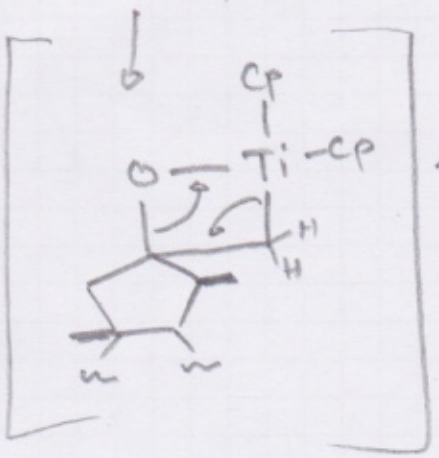




Q7:

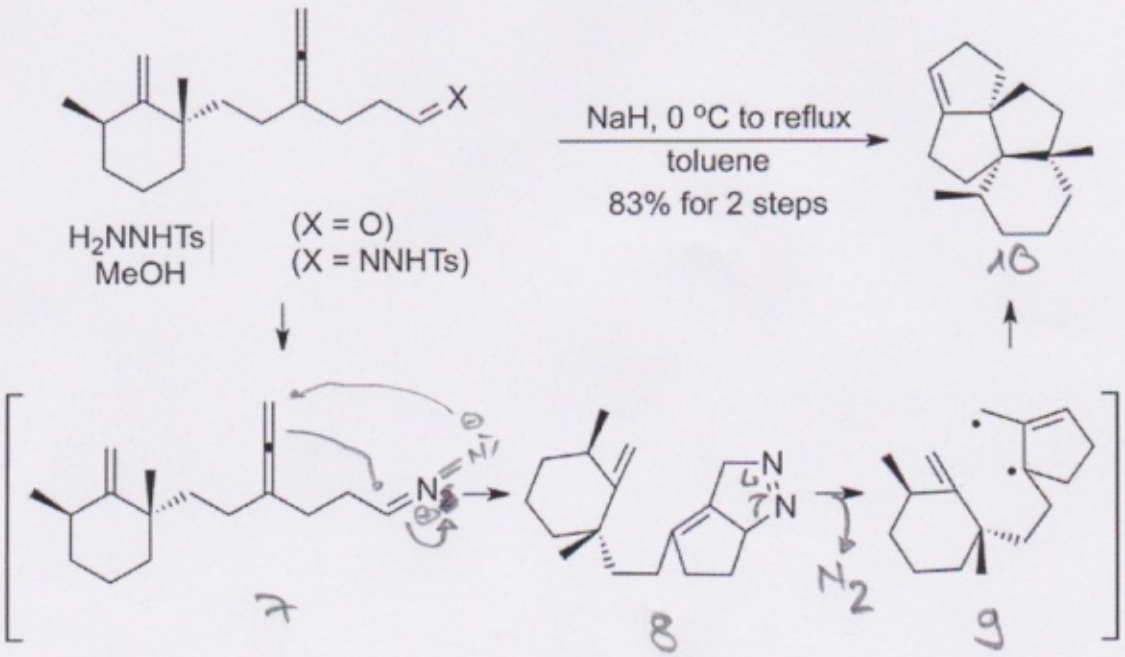


Waihoensene

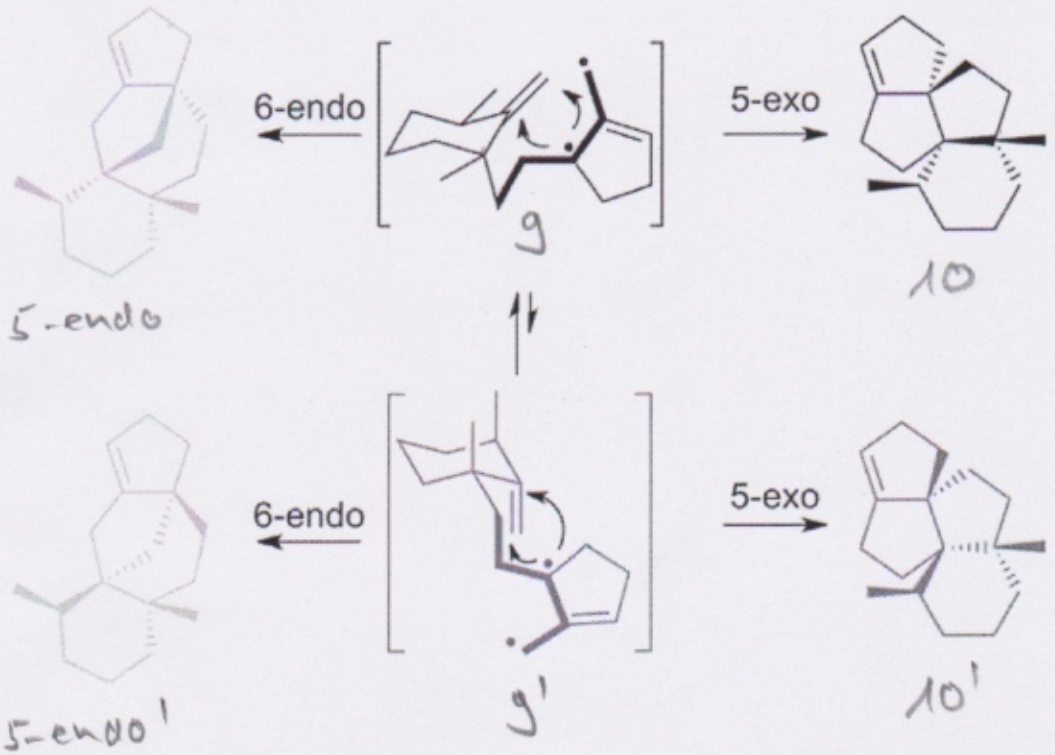


Co Petasis-reagent would also methenylate the ester-group in (1)

Q5:


X
H2NNHTs
MeOH
(X = O)
(X = NNHTs)
NaH, 0 °C to reflux
toluene
83% for 2 steps
10
7
8
9
N2

Q6:


6-endo
5-exo
9
10
5-endo
6-endo
5-exo
9'
10'
5-endo'