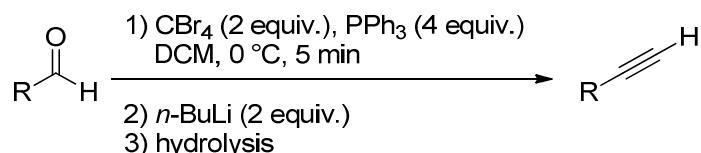


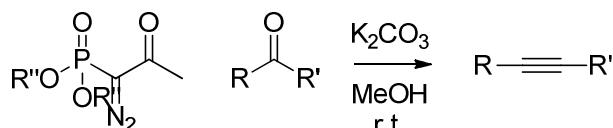
ALKYNES

I. Mechanisms: preparation and use of alkynes

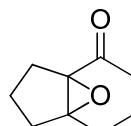
1) Corey-Fuchs alkyne synthesis



2) Seydel-Gilbert homologation (with use of the Ohira & Bestmann reagent)



3) Eschenmoser-Tanabe fragmentation



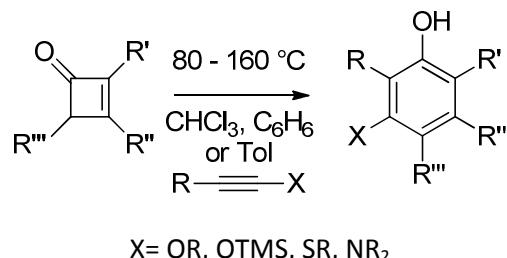
N.B.: The reaction conditions are quite similar to that of a Shapiro reaction.

5) Brown hydroboration and oxidation:

Substitute the boron of a vinyl borane with a hydroxy- or an amino- group. Reagents and mechanisms. Alternatively, how would you get the other regioselectivity for the ketone formation.

6) Electrocyclic reactions:

- Danheiser benzannulation reaction



Mechanism. Can you think of another starting material / conditions to afford the same type of reaction.

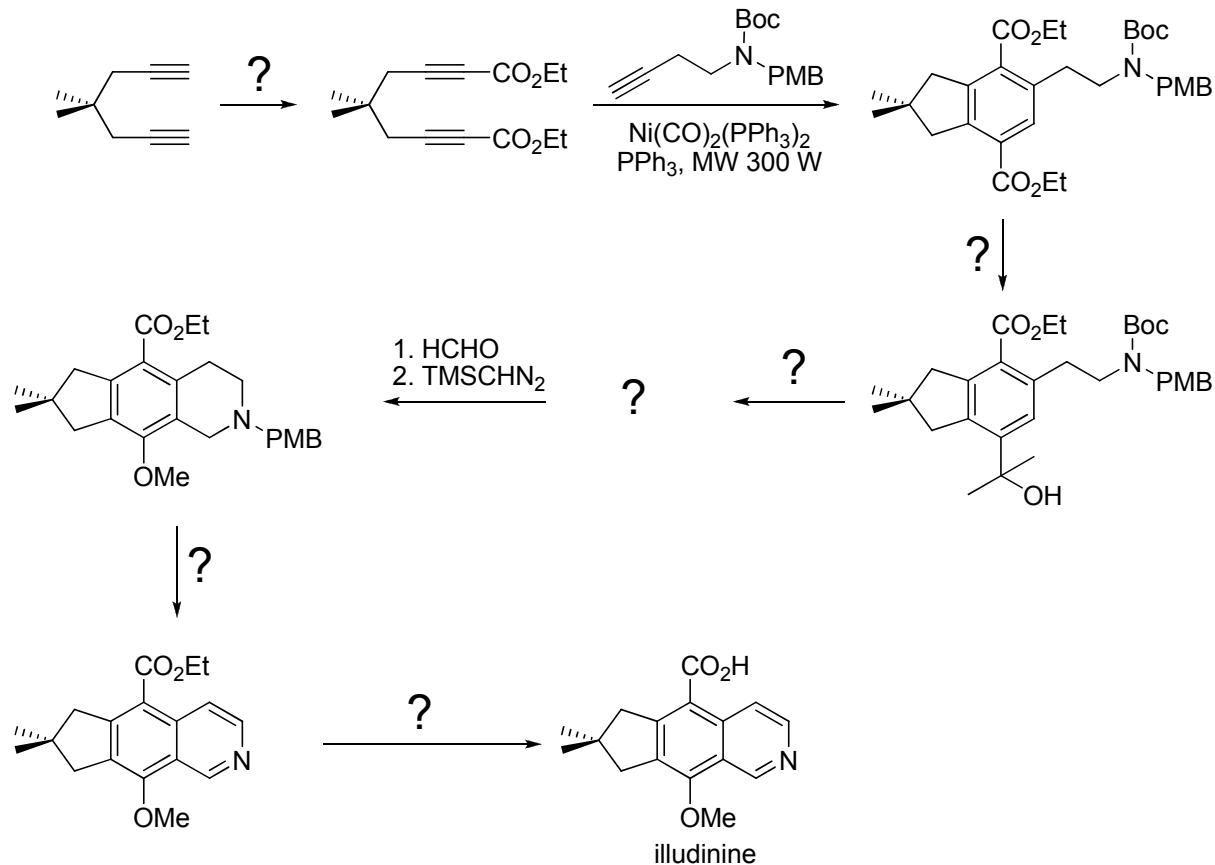
7) Larock indole synthesis

It is a one-pot Pd-catalysed reaction between an *o*-iodoaniline and an internal alkyne (needs a source of chloride). Mechanism.

II. Total synthesis

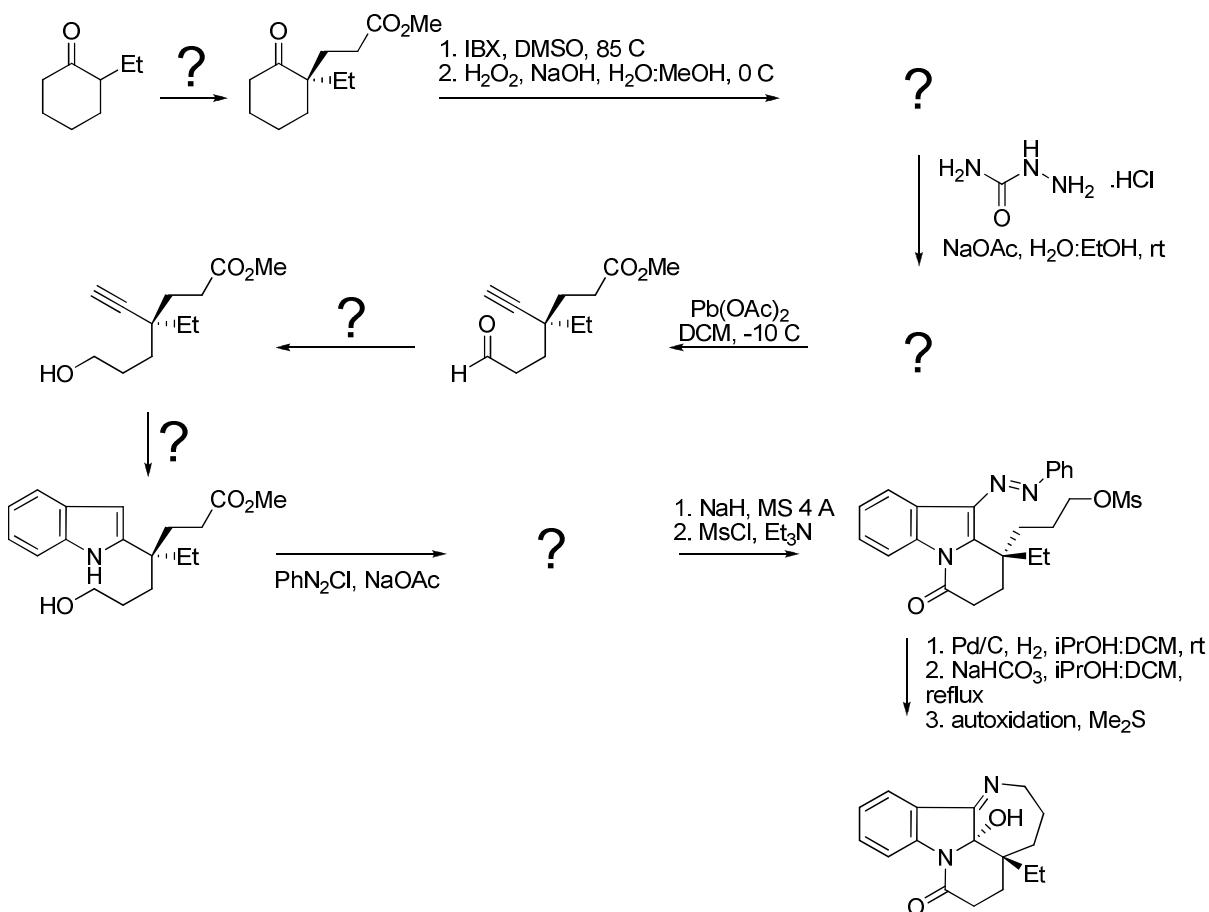
1) Jesse Teske and Alexander Deiters's total synthesis of Illudinine (2008).

Complete the missing reagents, products and mechanisms.



2) Nakajima, Ogino, Yokoshima and Fukuyama's synthesis of (-)-Mersicarpine (2010).

Complete the missing reagents, products and mechanism.



III. Retrosynthesis.

This is the retrosynthesis analysis of macbecin I made by Belardi and Micalizio. Draw the synthesis starting with **4** (for the bit between cuts a and b) and with **5** (for the aldehyde bit of **3**).

