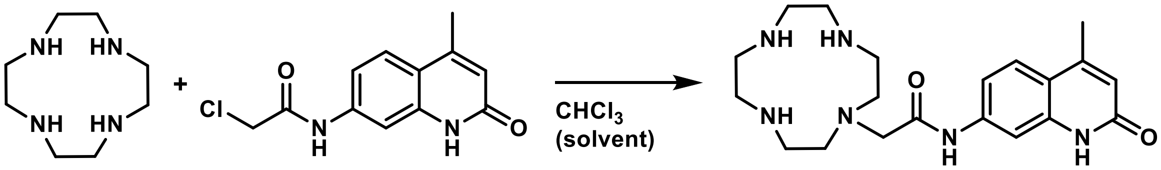
Homework 5 – 2017/05/03

1) A PhD student carries out the following reaction:



a) Identify the nucleophile and the electrophile!

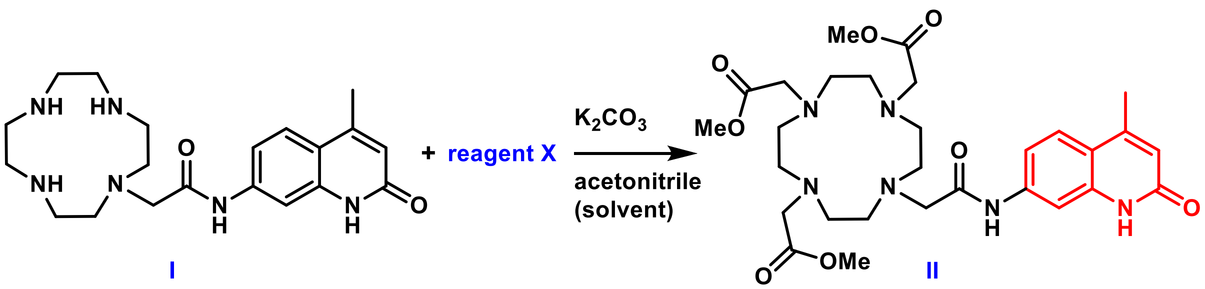
b) Draw the mechanism of the reaction!

c) What type of reaction is this?

d) What is (are) the by-product(s)? What happens to them during the reaction? Is their formation a problem for this reaction?

e) Do you expect any side-products to form? (I mean stuff that this poor student really would not wish to see forming.)

2) After successfully performing the reaction, the student took the product (**I**) and used it to prepare a new compound (**II**).



a) What is **reagent X**?

b) Draw the mechanism.

c) How many equivalents of K_2CO_3 do you need?

d) Identify the functional groups in **I** and **II**.

e) In what region do you expect the part highlighted in **red** to absorb (λ_{max})? If you need help, compare it to the structures in Homework 3.

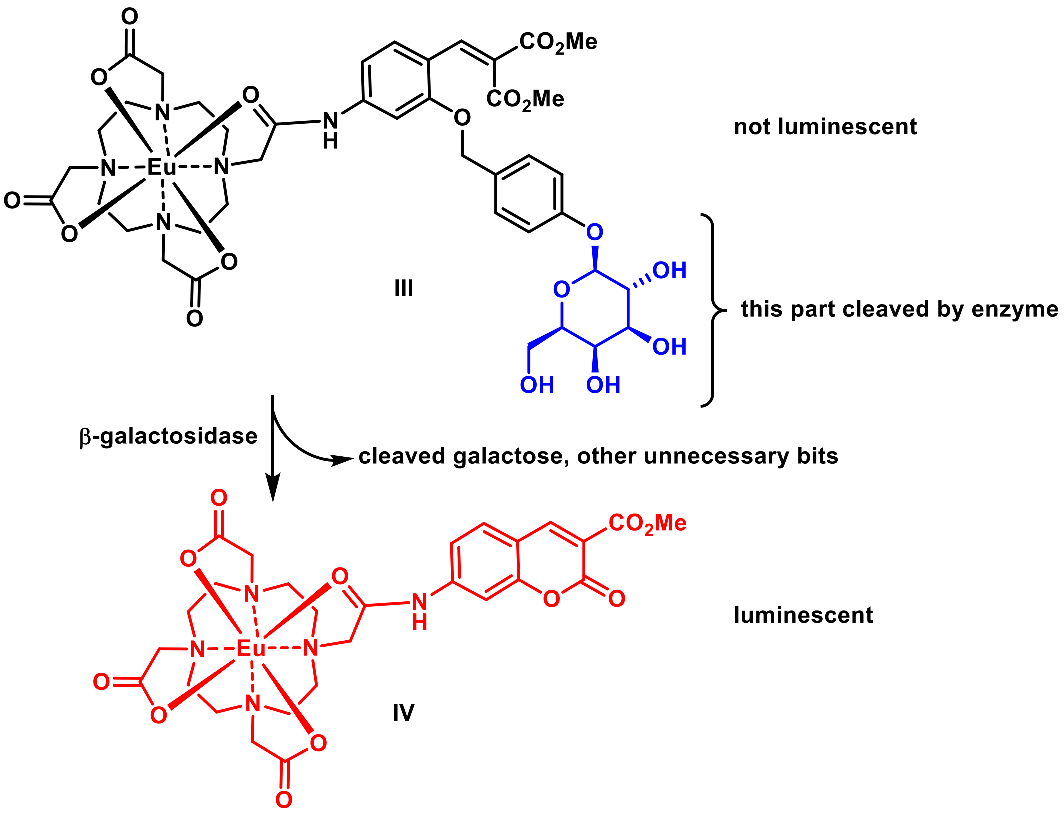
f) You can hydrolyze the methyl esters to the carboxylates ($RCOO^-$) with aqueous NaOH solution. Draw the product and the hydrolysis mechanism! Why do you form the carboxylates under these conditions, and not the carboxylic acids (RCOOH)?

g) Do you expect the final product to dissolve in water? Why or why not?

3) The final product in 2) can bind lanthanide ions[1]. These complexes are luminescent, which means that if you excite them with a photon, you get back a photon of a different color. The color is unique for the metal ion (**Figure 1**). In addition to being really pretty, these complexes are useful for studying biological processes. An example is given below.

Figure 1. Lanthanide complexes under a UV-lamp. Irradiation with UV-light (365 nm) results in the emission of red photons from a Eu-complex (left), and green photons from a Tb-complex (right). Photo by Daniel Kovacs.

β-galactosidase is an enzyme that cleaves **β-D-galactose** units from biomolecules. It is quite relaxed about its substrates, and can chop off the same group from non-natural compounds, like complex **III**, giving **IV**. Complex **IV** emits red light when excited, signaling that there is active β-galactosidase in the system.



a) Draw the Fischer projection of the open-chain forms of D-galactose and L-galactose.

b) Draw the pyranose forms (chair) of β-D-galactose, α-D-galactose, β-D-glucose, and β-D-mannose (see Table 16.1 for D-aldoses; page 428 in the 2nd edition).

[1] You *knew* this was coming, right?

c) What is the relationship between α-D-galactose and β-D-galactose?

d) What is the relationship between α-D-galactose and β-D-mannose?

e) What is the relationship between β-D-glucose and β-D-mannose?

f) Draw the possible pyranose and furanose forms of D-idose.

4) If you put live bacteria in a solution containing Ln complexes similar to **III**, after a while you will find some of the complex inside the (still live!) cells. Our initial hypothesis was that the cellular uptake was due to the β-D-galactose unit. Maybe **III** was mistaken for food.[2]

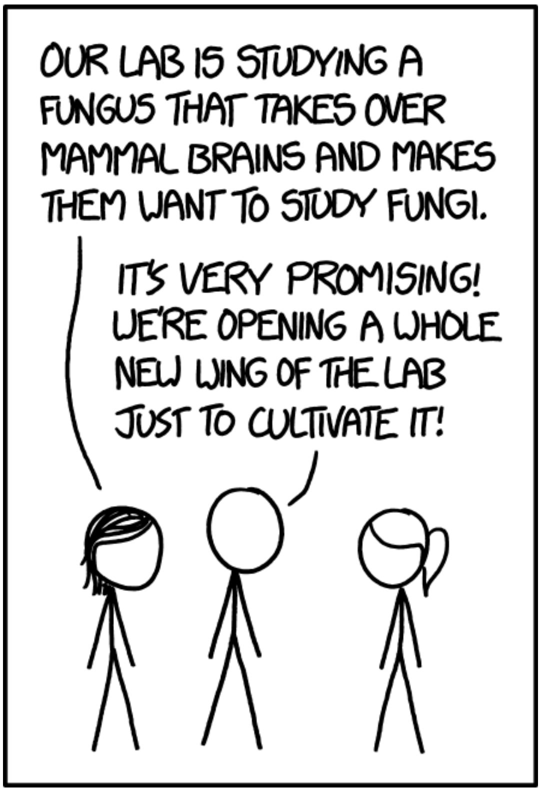
a) How would you test this hypothesis? You can assume to have access to any instruments or chemicals you need, and the PhD student can make any fancy compounds.

b) Surprisingly, even complexes lacking a sugar are taken up, through what seems to be active transport. How would you, a biologist, try to figure out what is happening?

Solutions can be handed in to Daniel Kovacs or to me in person, or you can mail them to eszter.borbas@kemi.uu.se

As long as you attempt to answer at least one question you will get feedback.

/Eszter[3]



[2] You know, it looks kinda like a sugar, plus there was a big party last night and all that…
[3] Some of the problems are based on my group's research, you can ask Dani or me for details.