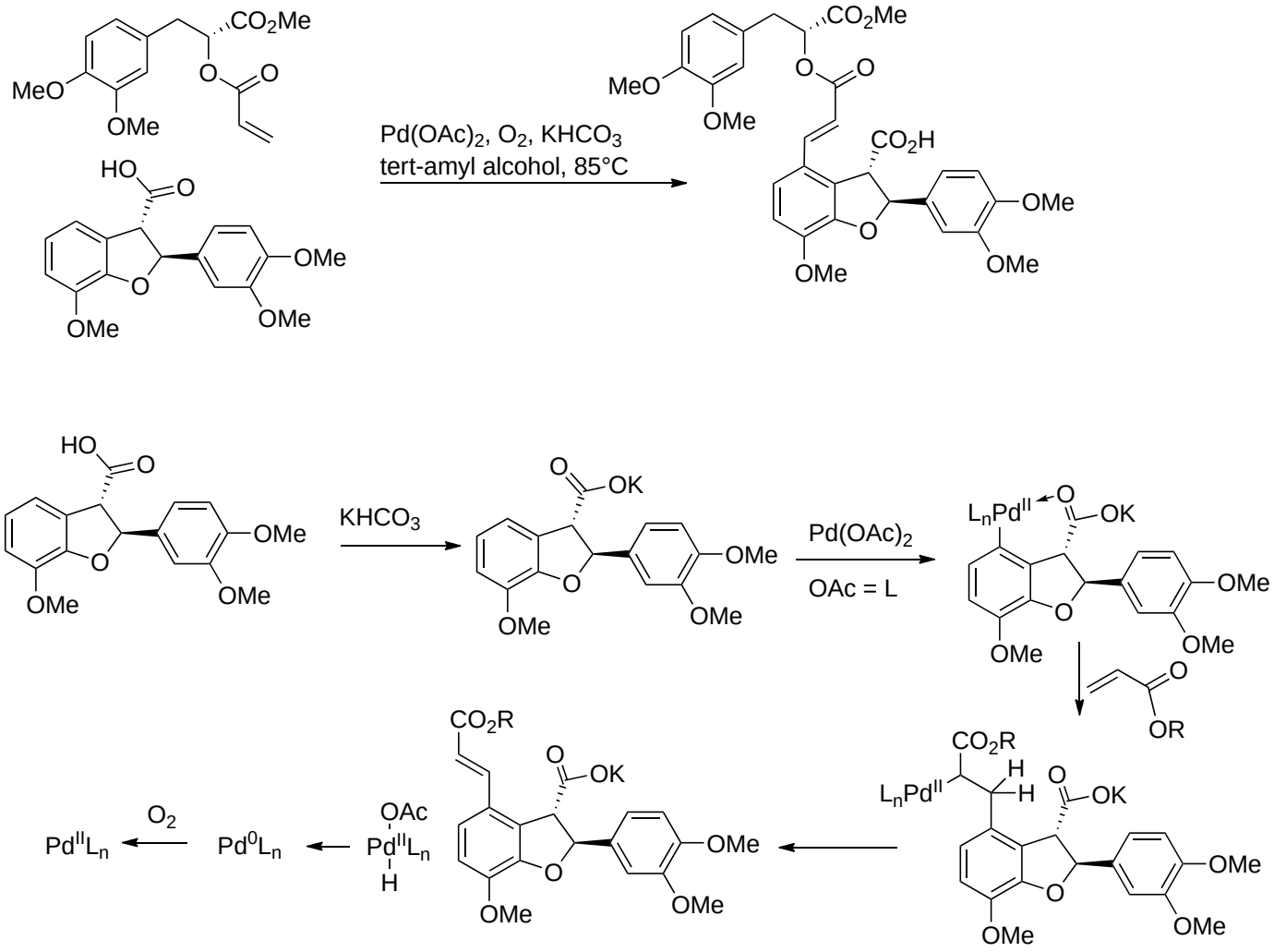
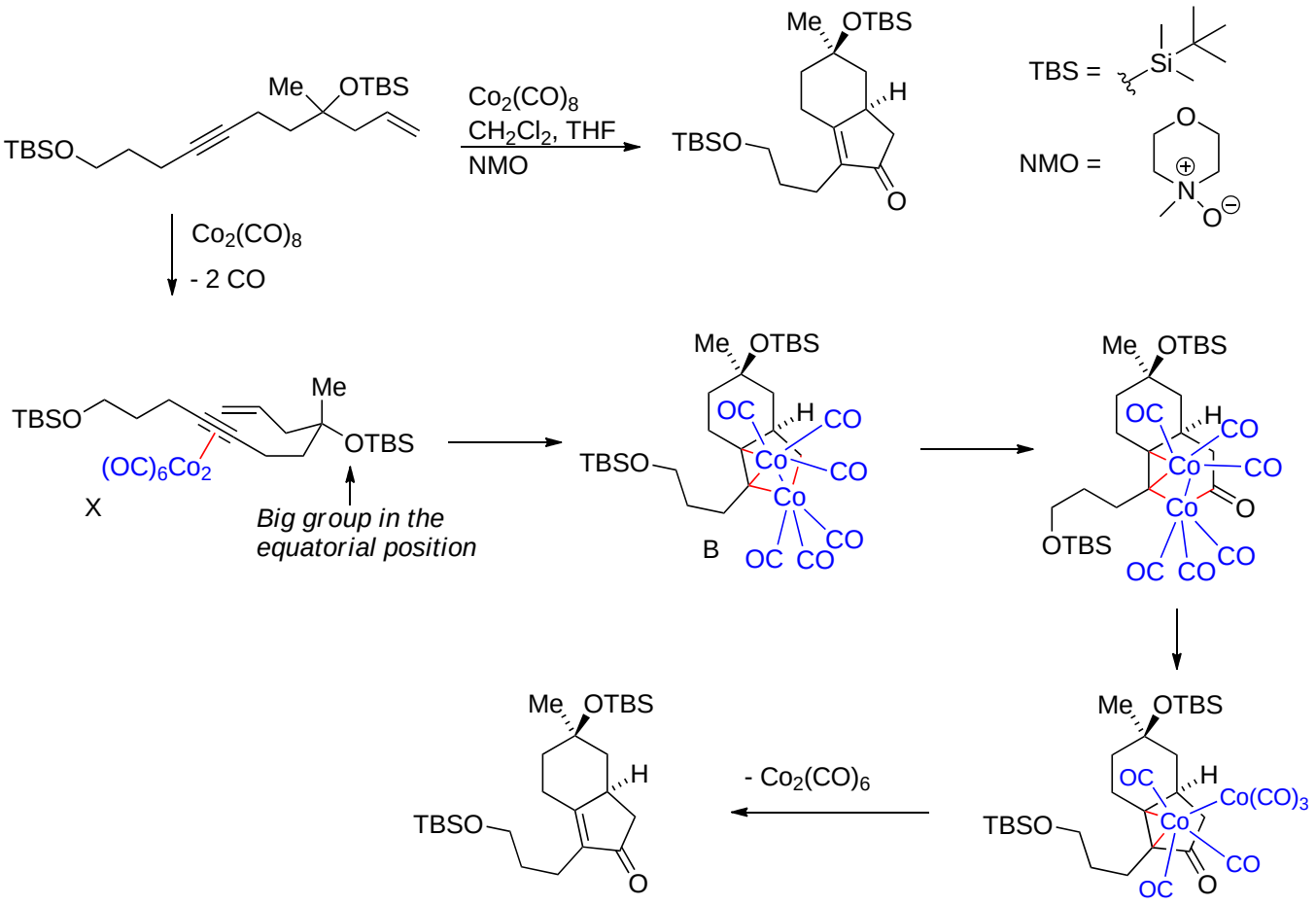
POW 12 - Solutions

What is the structure of **A**? Provide a reasonable mechanism, showing the most relevant intermediates.



The transformation belongs to the oxidative Heck-reactions proceeding by a C-H activation. Initially the carboxylic acid is deprotonated. The carboxylate is a competent directing group initiating the cyclometalation with the Pd(II)-catalyst. Next, a migratory insertion occurs, incorporating the acrylic ester in a 1,4-type addition. A beta-hydride elimination restores the double bond and releases the product. At the same time the Pd(II)-hydride complex reductively eliminated acetic acid to give a Pd(0)-species which is in turn oxidized back to the initial Pd(II)-catalyst by molecular oxygen.

Illustrate the shown process by characteristic intermediate. **B** is formed with a dr of 97:3.
Try as well find an argument for this outcome.



The process is a classic example of a Pauson-Khand reaction. First, the dicobaltoctacarbonyl coordinates to the alkyne, loosing to CO ligands. The stereo-determining step is the shown intermediate **X**. The large OTBS-group is preferentially positioned equatorially. Next, olefin inserting leads to the intermediate metallocycle **B**. This step is followed by the insertion of a CO ligand. Reductive elimination closes the five-membered carbocycle. In the final step decomplexation of dicobalthexacarbonyl gives the double bond. This step is accelerated by NMO.