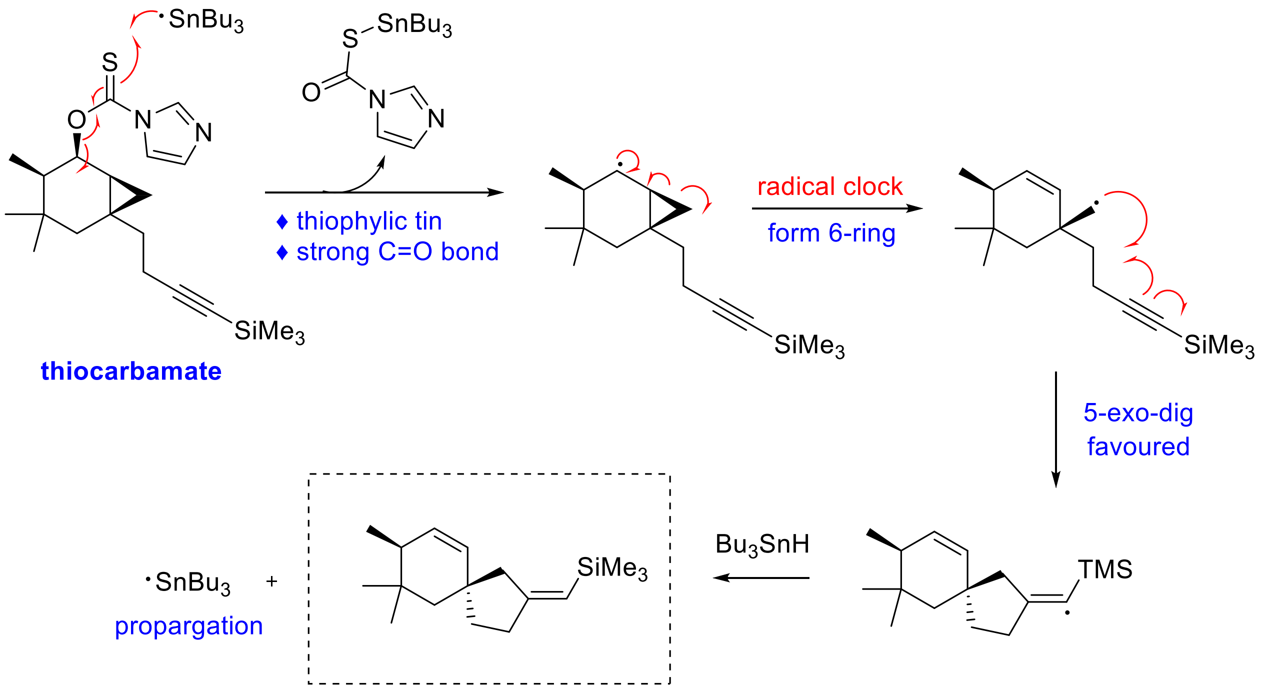
SR2025 POW9 Solution

1) *First:*

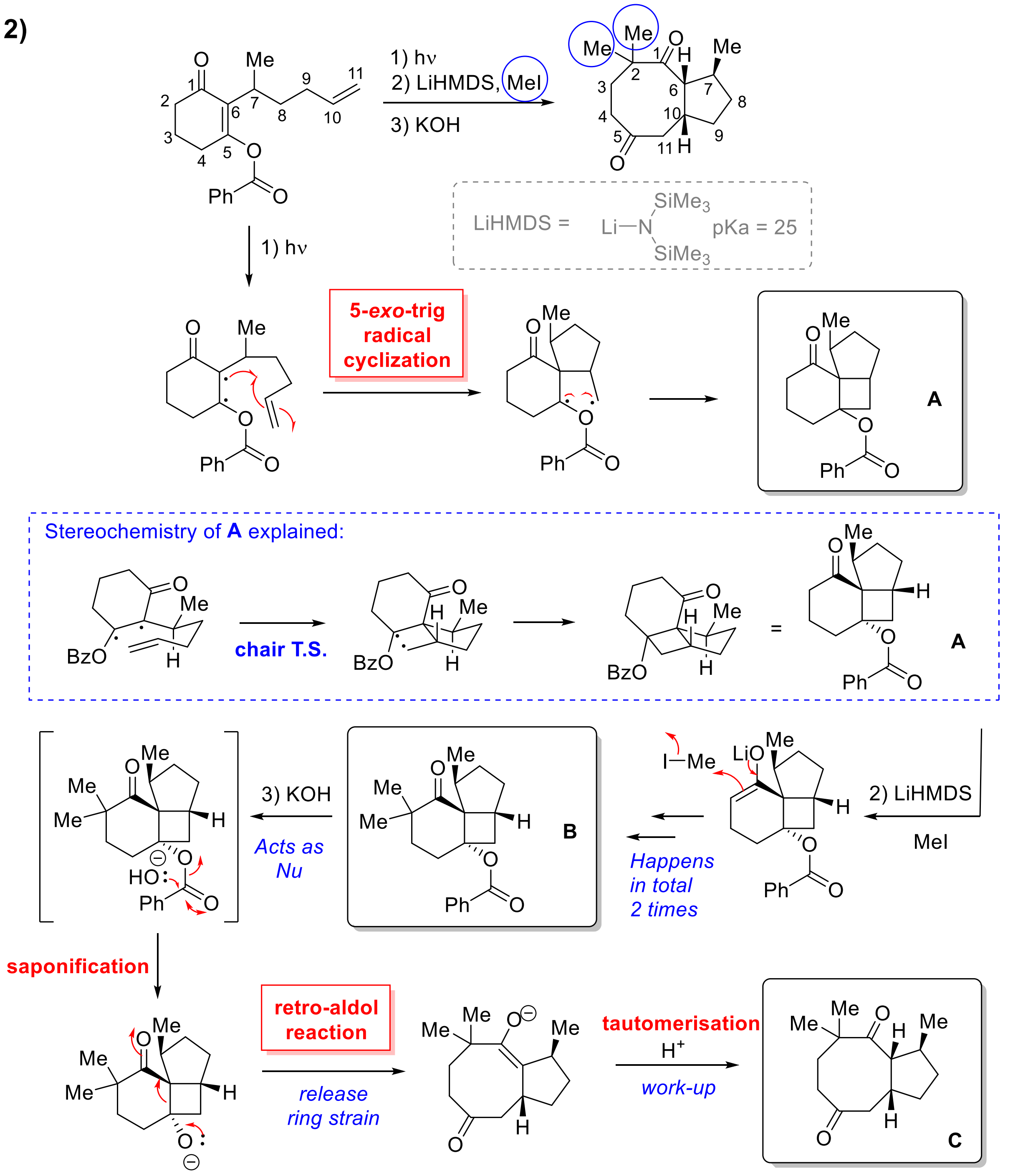
Benzoylperoxide forms under heat a phenylradical + CO_2 (weak peroxide bond, 139 kJ/mol) and in this way initiates the radical reaction (by abstracting a H radical from $HSnBu_3$).

Then:



This is a variation of the **Barton-McCombie deoxygenation** (originally with a xanthate ester).
The initial thiocarbamate-FG can be formed by e.g. reacting an alcohol with TCDI (thiocarbonyldiimidazole).

2)



Numbering of the starting material and the product reveals that several bonds need to be made and broken:

- The only missing atoms in the starting material are the two metyl groups, which have to come from MeI.
- The benzyl ester has been removed in the product.

In the presence of light, activation of the conjugated system is the most probable reaction. Using the simplified model of a biradical, a fast 5-exo-trig radical cyclization is now possible. The typical chair transition state with the methyl group in equatorial position explain the *cis* relationship between the proton and the methyl group. The relative stereochemistry to the OBz group is given by the geometry of the starting material and the orientation of the enone system to form a four membered ring directly.

The second step is a double methylation of the alpha position of the ketone.

The last step begins with a saponification of the ester, followed by a retro-aldol reaction, driven by the release of ring strain. Protonation during work-up then gives tautomerisation to the thermodynamically more stable ketone.