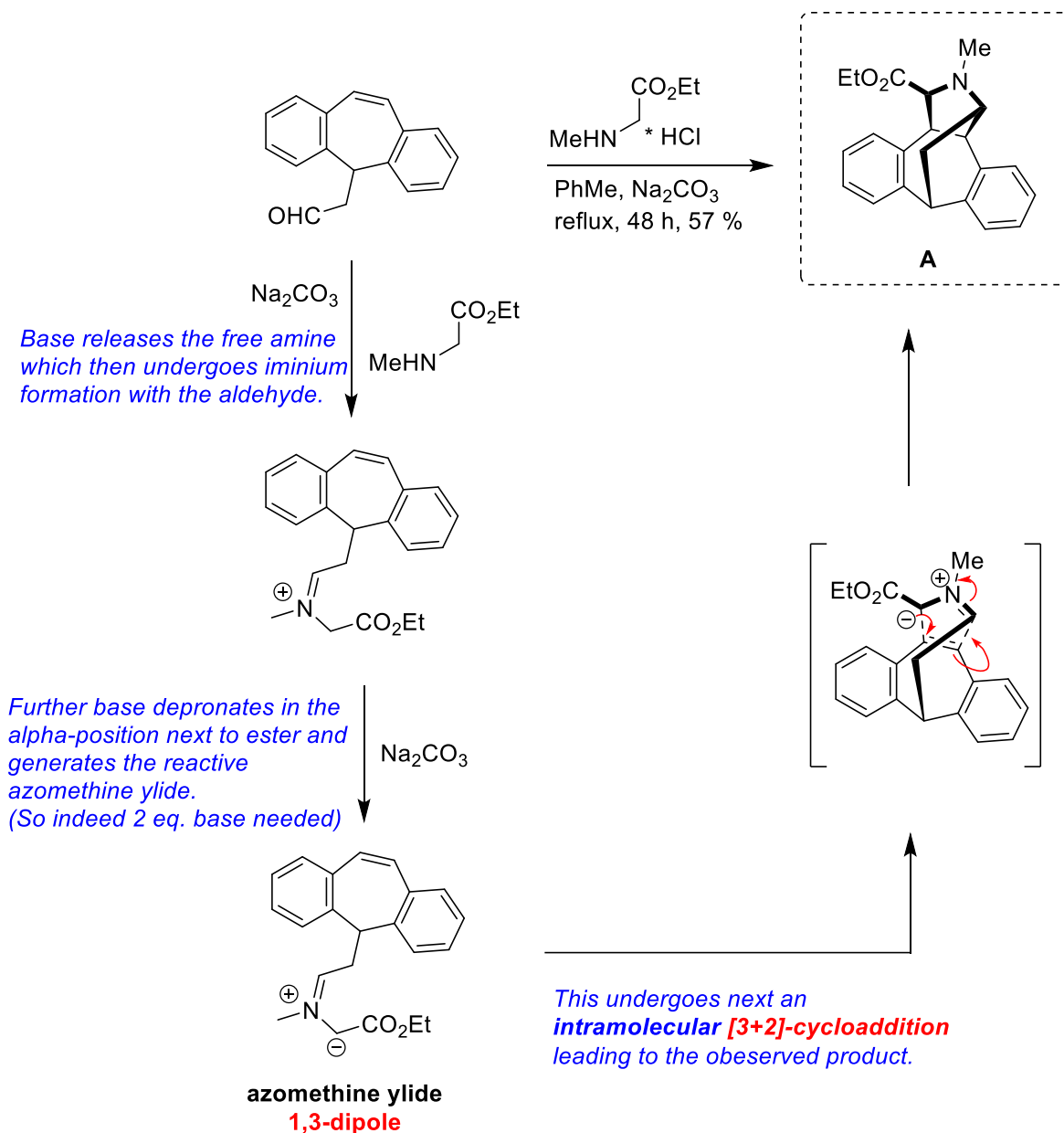
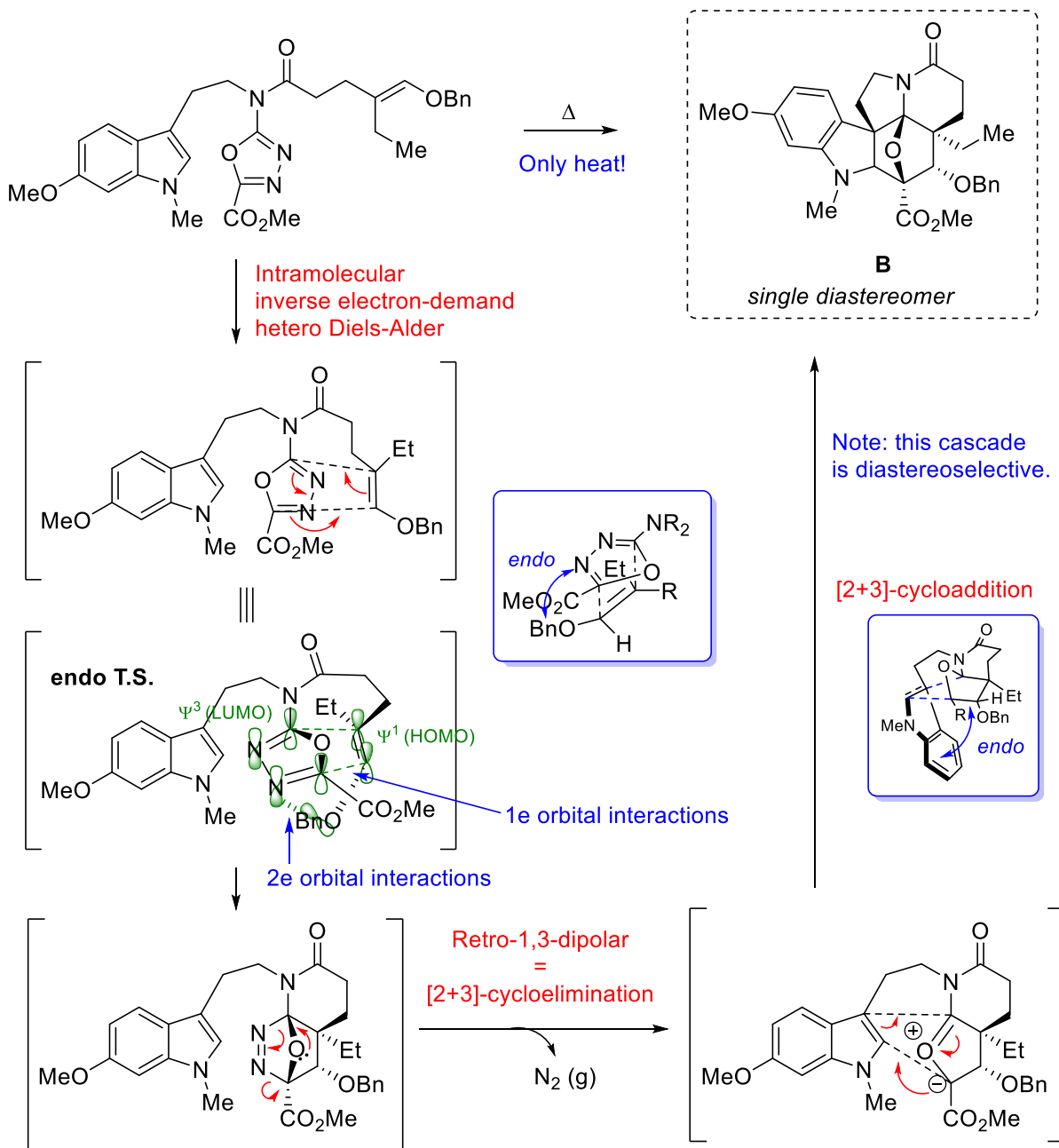


SR2025 - POW 7 - Solutions

1) Explain the shown transformation and draw the relevant intermediates?



2) Identify the different cycloadditions, and draw all relevant synthetic intermediates.



For [4+2]-cycloaddition:

- 1,3,4-oxadiazole reacts with electron-rich enol ether.
- Inverse e-demand, so now LUMO of diene (e-poor) with HOMO of dienophile (e-rich), as depicted.
- Substituents in both diene and dienophile complement and reinforce the [4+2]-addition's regioselectivity, which is already dictated by the linking tether.
- The stereoselectivity is controlled by the dienophile's geometry (due to tether), and additionally for the shown (*E*)-olefin (OBn and Et on same side) it is also via the *endo* T.S. (OBn is inside the "boat" for secondary orbital interactions).

For [2+3]-cycloelimination:

- Formation of carbonyl ylide **1,3-dipole**.
- Driven by release of nitrogen gas.
- 1,3-dipole is stabilised by the appropriate EWG (CO_2Me next to \ominus) and EDG (NR_2 next to \oplus) at both termini.

For [2+3]-cycloaddition:

- Exclusive *endo*-indole T.S.
- Again, likely this is strain-driven by the tether.
- Also here, the [3+2]-addition's regioselectivity is dictated by the tether, but the 1,3-dipolarophile (indole) complements it (δ^- next to δ^+).