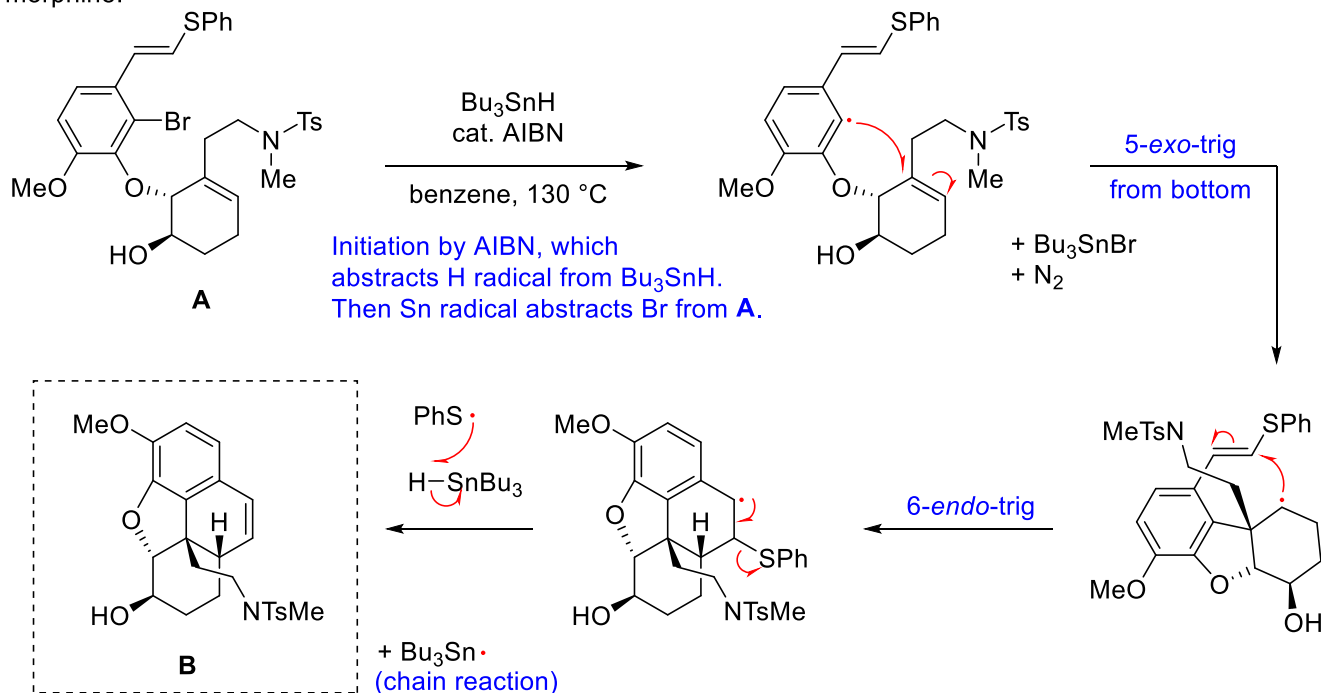


SR-2024 POW-8 - Solution

- 1) A radical cascade reaction on **A** leads to **B**, which is an advanced intermediate in the total synthesis of morphine.



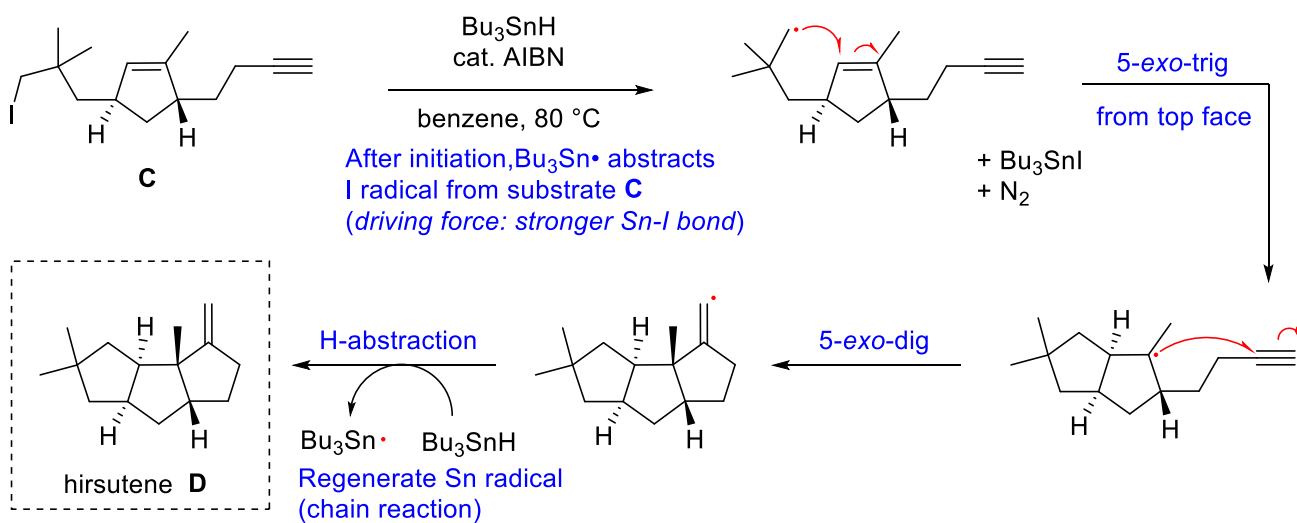
For first cyclization:

Attack by the aryl radical happens to the bottom face of the alkene, because of the fixed stereochemistry of the ether linkage.

For second cyclization:

We do not get the, otherwise in general kinetically favoured, 5-exo-trig cyclization, because of geometric constraints imposed by the tricyclic framework.

- 2) The outlined reaction of **C**, leading to hirsutene **D**, belongs to the classics in total synthesis.



3) Following transformation is part of Nobel laureate E. J. Corey's total synthesis of perhydrohistrionicotoxin.

