Sn2 is not possible due to steric hindrance (the nucleophile would have to pass through the ring) and due to repulsion from the π system.

Sn1 is not possible because the resulting change in hybridization (sp² → sp) would be unfavorable geometrically and would form a carbocation at a vinyl position, which is unfavorable due to the large s-character of the orbital.

Nucleophilic Aromatic Substitution is delocalized off the ring.

What helps an electrophilic addition hurts a nucleophilic addition.
Diels-Alder reaction: \( \rm{[4+2]} \) cycloaddition

diene

Diels-Alder reactions can only occur if the \( \pi \) bonds are in a **pseudo-cis** configuration.

\( \text{rotation around} \quad \text{single bond not} \quad \text{\( s\)-cis restricted} \quad \text{\( s\)-trans} \)

If the top carbons on either molecule were close enough to react, the bottom carbons would not be.

If a diene is "locked" into a **\( s\)-cis** configuration, it would be a lot more reactive than a comparable diene.

Cyclopentadiene is reactive enough that it naturally occurs as a dimer (two of the same atom/molecule bound together).

If a diene is locked into a **\( s\)-trans** configuration, it will be unreactive.

* In Diels-Alder reactions, the diene must be conjugated.
ground state!

Homo

LUMO

phases match